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ALLYL AND NITROSYL COMPOUNDS OF TRANSITION METALS

by



NOBUKAZU OKAMOTO

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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The undersigned certify that they have read, and
recommend to the Faculty of Graduate Studies for
acceptance, a thesis entitled

"ALLYL AND NITROSYL COMPOUNDS OF TRANSITION METALS"

submitted by NOBUKAZU OKAMOTO in partial fulfil-
ment of the requirements for the degree of Doctor
of Philosophy.

A B S T R A C T

A number of π -allyltricarbonyliron derivatives of germanium and tin have been synthesized by halide displacement from organometallic halides with the π -allyltricarbonyliron anion. These compounds have the general formula, $R_3MFe(CO)_3(\pi-C_3H_5)$ or $R_2M[Fe(CO)_3(\pi-C_3H_5)]_2$ (where R is Me, Ph or halogen, and M is Ge or Sn). Some of these compounds were found to exhibit more bands in the carbonyl stretching region than there were carbonyl groups in the molecule. This was interpreted in terms of conformational isomerism involving rotation about an axis through the π -allyl plane and/or rotation about the Fe-M bond. Evidence for the presence of two conformers with respect to the π -allyl moiety was obtained by studying the NMR spectra over a range of temperatures.

Many transition metal nitrosyl derivatives have also been prepared by the reaction of transition metal carbonyls or their derivatives with nitrosonium hexafluorophosphate in acetonitrile. Chromium hexacarbonyl gave the new cation, trans- $[Cr(NO)_2(MeCN)_4]^{++}[PF_6]_2^-$, whilst molybdenum and tungsten hexacarbonyls produced the corresponding cis cations. The carbonyl containing cation, cis- $[W(CO)(NO)_2(MeCN)_3]^{++}[PF_6]_2^-$ was isolated as an intermediate in the formation of the dinitrosyl tungsten derivative. These compounds, isolated as hexafluorophosphate salts,

were found to react with a variety of ligands, with displacement of acetonitrile, to produce either ionic or neutral compounds which constituted a new series of dinitrosyl derivatives of chromium, molybdenum, and tungsten. Infrared, NMR, and mass spectroscopic studies of the latter new compounds were presented.

Reactions of nitrosonium hexafluorophosphate have been found to provide superior methods for the synthesis of the known compounds $\text{Mn}(\text{CO})_4\text{NO}$, $\text{Co}(\text{CO})_3\text{NO}$, $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}]^+$ and $[\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2\text{NO}]^+$. Also found in nitrosonium salt reactions were the new ionic species $[\text{MeCNMn}(\text{CO})_5]^+$, $[\text{MeCNRe}(\text{CO})_5]^+$ and $[\text{Re}_2\text{O}(\text{CO})_6(\text{NO})_2(\text{MeCN})_2]^{++}$. The latter is believed to contain a linear Re-O-Re bond and it has been converted to the neutral $(\text{acac})_2\text{Re}_2\text{O}(\text{CO})_4(\text{NO})_2$ (acac = acetylacetonate anion).

A C K N O W L E D G E M E N T S

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A B B R E V I A T I O N S

The following list of abbreviations will be employed in this Thesis. All temperatures are °C.

acac	acetylacetonate anion
dipy	2,2'-dipyridyl
diphos	bis(1,2-diphenylphosphinoethane)
Et	ethyl, C_2H_5
hfac	1,1,1,5,5,5-hexafluoroacetylacetonate anion
L	ligand
Me	methyl, CH_3
MeCN	acetonitrile, CH_3CN
n-Pr	n-propyl, $CH_3CH_2CH_2$
Ph	phenyl, C_6H_5
PPh_3	triphenylphosphine
PMe_2Ph	dimethylphenylphosphine
tfac	1,1,1-trifluoroacetylacetonate anion
THF	tetrahydrofuran

CHAPTER I

A Review of Compounds Involving Bonds Between the Allyl Group and Transition Metals

Many compounds are known in which the allyl group is bonded to transition metals. These compounds may be classified as σ -allyl(σ -C₃H₅) and π -allyl(π -C₃H₅) compounds.

In the σ -allyl compounds, the allyl group contributes one electron to the metal-allyl bond to give a carbon-metal electron pair bond. In the π -allyl compounds, the allyl group may be regarded as a three-electron donor. Both σ -allyl and π -allyl compounds have been reviewed by Green and Nagy (1) and the crystal structures of a number of π -allyl derivatives have been briefly discussed by Churchill and Mason (2). What follows owes much to these reviews, and is not intended to be an exhaustive survey of previous work in this field.

Part of the work described in this Thesis involves π -allyltricarbonyliron derivatives, and this particular area will be discussed in detail in Section 3.

1. σ -Allyl transition metal compounds.

σ -Allyl transition metal compounds are prepared by following two main routes:

- (a) Reaction of sodium salts of metal carbonyls with allyl halides, e.g.,



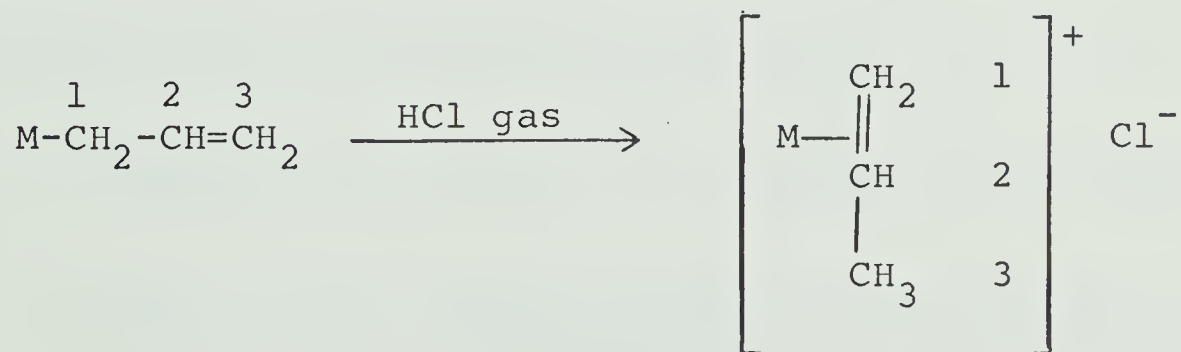
(b) Reaction of metal hydrides with conjugated dienes,
e.g.,



The latter reaction involves 1,4 addition of the H-Mn bond across the diene, the product being a mixture of cis and trans isomers (3).

Both methods involve standard methods for preparation of metal-carbon σ -bonds. All the known σ -organotransition metal compounds in which the organic ligand has an unsaturated β -carbon atom form yellow to yellow-brown oils which are very air-sensitive and are thermally unstable.

A number of σ -allyl transition metal compounds are readily protonated by dry hydrogen chloride to afford cationic species containing propene as a ligand; M in this equation may be $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ (4), $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3$ (5), and $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3$ (6). The mechanism proposed involves proton-

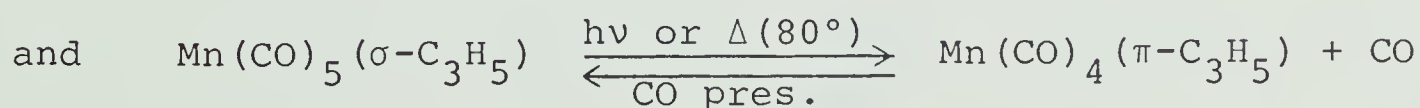
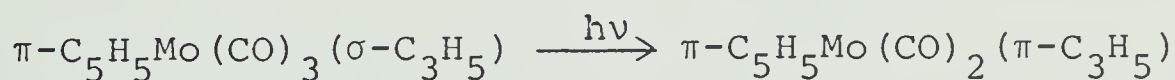


ation at the C-3 atom of the σ -allyl group resulting in an intermediate carbonium ion which may transfer its positive charge to the metal atom, and finally bond to it by a

π -bond. The protonation at the C-3 atom has been shown by deuteration experiments (7). In σ -allylmanganese pentacarbonyl, the protonation reaction proceeds a step further and the olefin is displaced affording $\text{Mn}(\text{CO})_5\text{X}$, where $\text{X} = \text{NO}_3^-$, CF_3COO^- , Cl^- , and HSO_4^- . However, if perchloric acid is used, the intermediate $[\text{Mn}(\text{CO})_5\text{C}_3\text{H}_6]^+$ species can be isolated (8,9).

These olefinic cations can also be prepared by hydride abstraction from σ -alkyl compounds using triphenylmethyl fluoroborate, and the hydride has been shown to be abstracted from the C-2 atom. However, reductions of these olefinic cations with sodium borohydride give only σ -isopropyl derivatives, and there is no evidence for the presence of the σ -n-propyl isomer (10).

Irradiation with ultraviolet light or mere heating of any of the σ -allyl transition metal compounds results in the displacement of carbon monoxide from the metal and formation of a π -allyl derivative, which may also be carbonylated under carbon monoxide pressure, e.g.,



It is interesting to note that as the metal changes from left to right in the periodic table, the decarbonylation of the σ -allyl metal compound becomes so easy that only

the π -allyl metal compound is isolated in the case of the cobalt analogue.

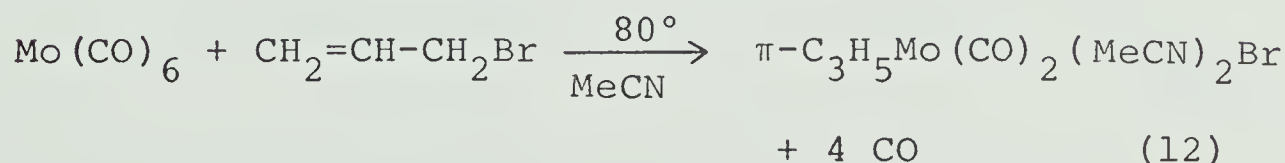
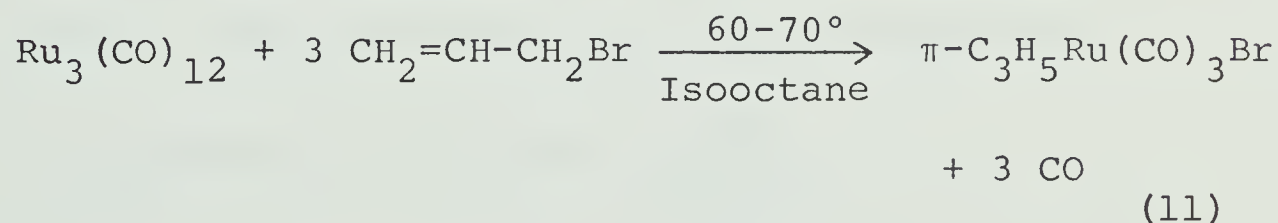
2. π -Allyl transition metal compounds

A number of compounds have been prepared in which the allyl group can act as a "half sandwich", and it can be regarded as a formal three-electron donor. These π -allyl transition metal compounds are prepared by the following methods:

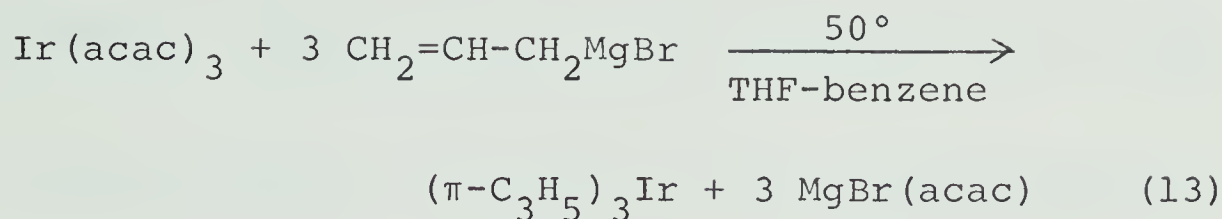
- (a) Reaction of sodium salts of transition metal carbonyls with allyl halides.

As discussed previously, this method gives rise initially to σ -allyl transition metal compounds which may readily lose one carbonyl group to form the π -allyl derivatives on warming, or in some cases under irradiation with ultraviolet light.

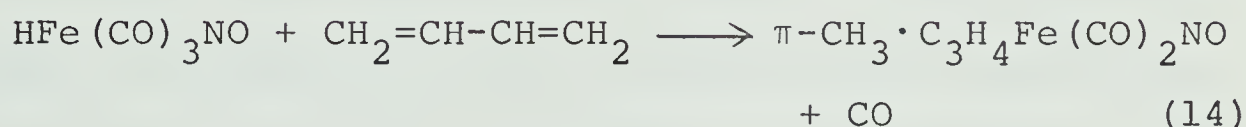
- (b) Reaction of metal carbonyls with allyl halides;



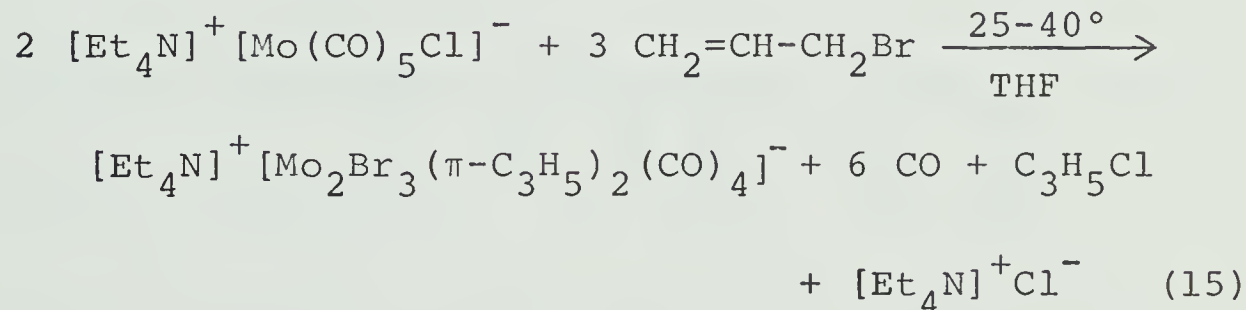
- (c) Reaction of metal salts with allyl Grignard reagent;



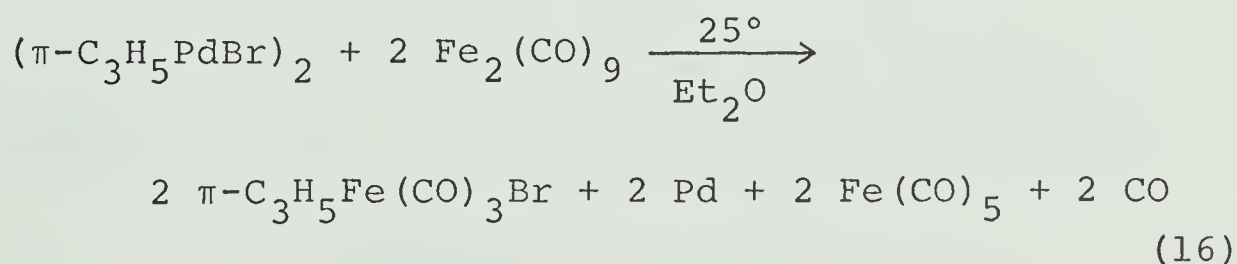
(d) Reaction of transition metal hydrides with dienes;



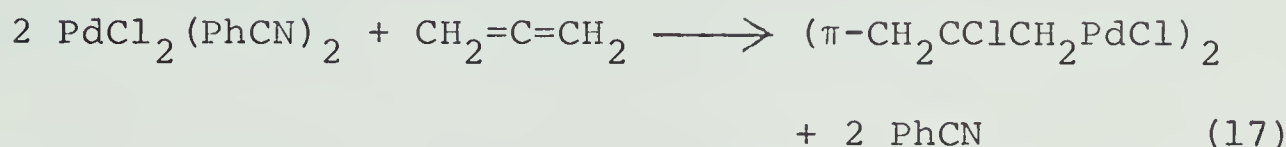
(e) Reaction of the tetraethylammonium salts of the halopentacarbonyl metal anions, $[\text{Et}_4\text{N}]^+[\text{M}(\text{CO})_5\text{X}]^-$ (where $\text{M} = \text{Mo}, \text{W}$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$), with allyl halides;



(f) Intermolecular migration reaction of the allyl ligand, often referred to as ligand migration;

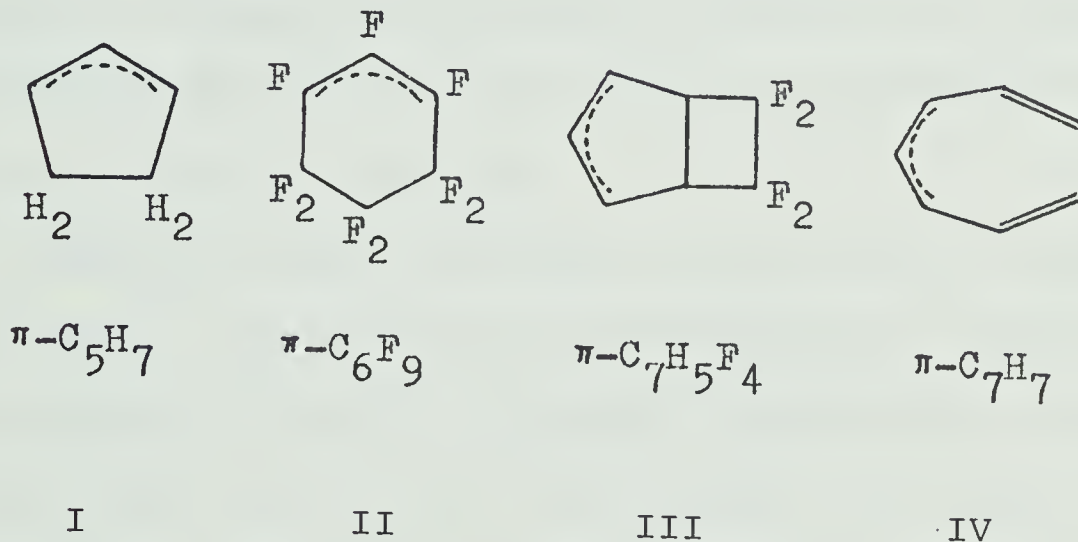


(g) Reaction of metal salts with olefins or allenes;

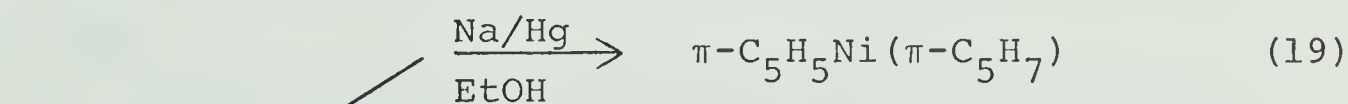


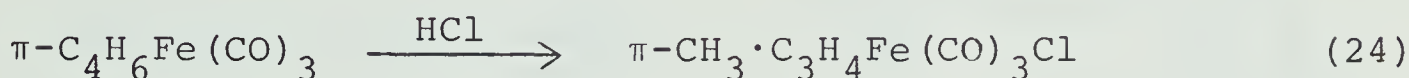
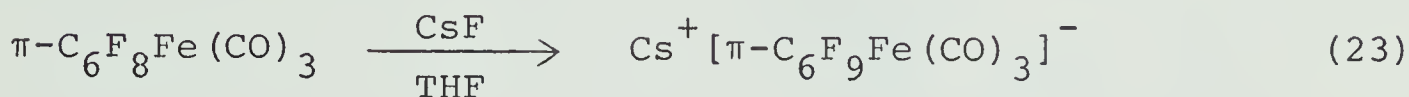
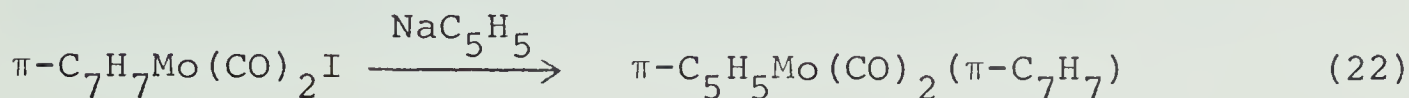
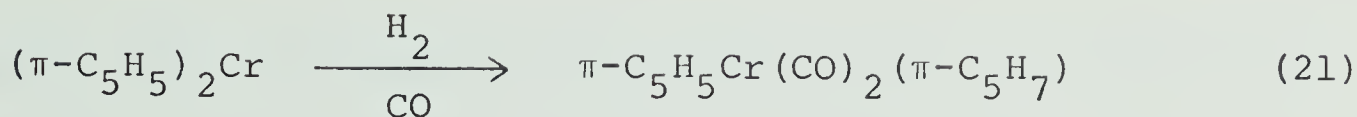
The latter reaction depends markedly on the reaction conditions. The action of allyl alcohol on palladous halides also gives the π -allyl, halide-bridged compound. Even direct reaction of palladium metal and allyl bromide affords the analogous bromine-bridged compound in 40% yield (18).

There are many examples of cyclic allylic ligands, such as the following:



Various methods of preparation for compounds containing these ligands are known, as the following reactions show:



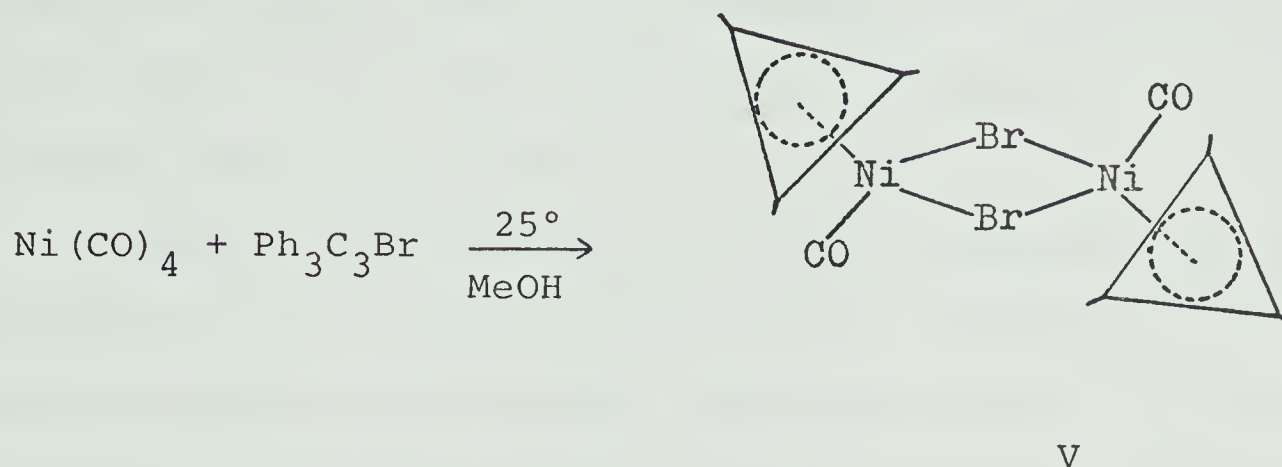


Some ionic π -allylic species have been reported. Treatment of (butadiene)tricarbonyliron with strong acids such as HBF_4 , HClO_4 , H_2SO_4 , affords cationic species in which the methyl group has the anti-configuration (25). Similarly, (trimethylenemethane)tricarbonyliron gives (π -methallyl)tricarbonyliron cation by protonation in concentrated sulfuric acid (26).

Transition metal compounds containing a π -bonded cyclopropenyl ring should be mentioned here, because the π -cyclopropenyl moiety is formally regarded as a three electron donor, as is the π -allyl group. Not many π -cyclopropenyl metal derivatives are known, although there seems no clear reason why the π -cyclopropenyl radical is not stabilized by forming a π -complex with a transition metal atom.

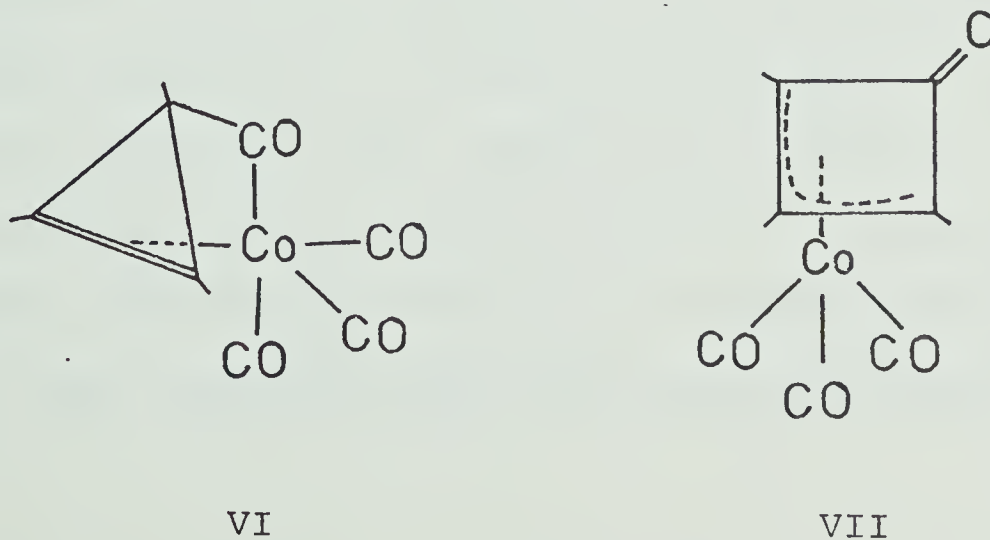
One way of obtaining these complexes involves the reaction of triphenylcyclopropenyl halides with metal carbonyls or their derivatives. Thus nickel tetracarbonyl

reacts with triphenylcyclopropenyl bromide to form π -triphenylcyclopropenylnickelcarbonyl bromide dimer (27):



Tris(acetonitrile)tricarbonylmolybdenum reacts with triphenylcyclopropenyl chloride to produce $(\text{MeCN})_2\text{MoCl}(\pi\text{-C}_3\text{Ph}_3)(\text{CO})_2$, which can be converted into $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_2(\pi\text{-C}_3\text{Ph}_3)$ by treatment with lithium cyclopentadienide (28).

The reaction between tetracarbonylcobalt anion with triphenylcyclopropenyl halides affords yellow, air-stable crystals of product, for which structure VI and VII have been proposed (29). The final Chapter of this Thesis describes the preparation of phosphine complexes of this compound.



Similarly, the isoelectronic tricarbonylnitrosyliron anion produces an analogous compound, $\text{Ph}_3\text{C}_3\text{Fe}(\text{CO})_3\text{NO}$ (29). Very recently the permethyl analogue $\text{Me}_3\text{C}_3\text{Co}(\text{CO})_4$ has been reported by King and Efraty who suggested the structure VII rather than VI for this compound (30), although the matter is still open to question.

Finally, the formation of allylic intermediates is believed to be of common occurrence in a variety of catalytic reactions such as the cyclotrimerization of butadiene to trans,trans,trans-cyclododeca-1,5,9-triene, the cyclooligomerization of butadiene and ethylene to 1,5-cyclooctadiene and trans,cis-1,5-cyclooctadiene by nickel catalysts (31), the carbonylation of conjugated dienes or arenes with carbon monoxide in the presence of palladous chloride (32), and the acylation of butadiene by acyl-tetracarbonylcobalt (33).

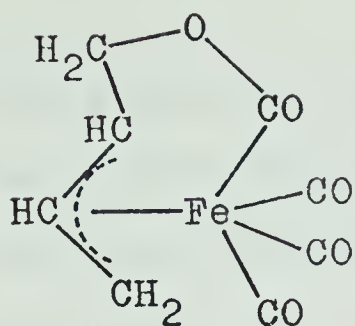
3. π -Allyltricarbonyliron derivatives

The first π -allyltricarbonyliron derivative was reported in 1961 by Impastato and Ihrman (24), who prepared 1-methyl- π -allyltricarbonyliron chloride by the reaction of hydrogen chloride on 1,3-butadienetricarbonyliron. Later, Emerson and Pettit (25) reported the 1-methyl- π -allyltricarbonyliron cation, prepared similarly by protonation of a double bond already involved in coordination to the iron atom; these reactions have been noted previously.

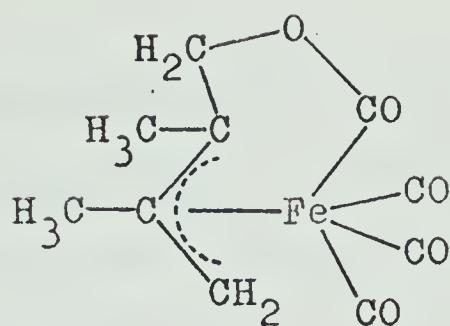
Plowman and Stone (34) described the preparation of π -allyltricarbonyliron iodides by the reaction of iron pentacarbonyl with allylic iodides at 40°. Murdoch and Weiss (35) reported an improved procedure for the synthesis of the parent π -allyltricarbonyliron halides, and also of π -allyl complexes with functional groups attached to the allyl ligand, by the reaction of diiron enneacarbonyl with allylic halides; this method is equally applicable to the preparation of the chlorides, bromides and iodides.

In 1964, Heck and Boss (36) reported the photochemical preparation of π -allyltricarbonyliron derivatives by ultra-violet irradiation of pentane solutions of allylic halides and iron pentacarbonyl at room temperature or below. They also reported a halogen-free complex from the reaction of cis-4-chloro-2-butene-1-ol for which structure VIII was proposed.

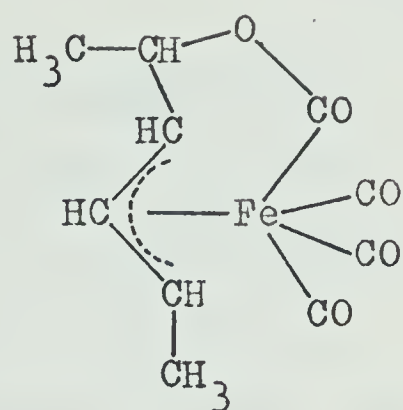
At the same time, Murdoch (37) prepared compounds VIII - XI by the reactions of allylic diols or allylic chloroalcohols with diiron enneacarbonyl and discussed their structures on the basis of spectroscopic and chemical evidence. A triphenylphosphine derivative of the compound VIII was also prepared by these authors.



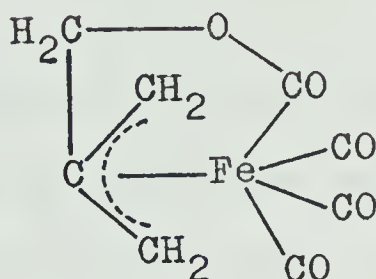
VIII



IX



X



XI

A novel fluoride addition to π -perfluoro-1,3-cyclohexadienetricarbonyliron was reported by Parshall and Wilkinson (23), who prepared the π -perfluorohexenyltricarbonyliron anion (as a cesium salt); this reaction has been noted previously.

Hübel and Braye (38) prepared an unusual and complicated binuclear phenylacetylene complex, $(\text{PhC}_2\text{H})_3\text{Fe}_2(\text{CO})_6$, by the reaction of diphenylacetylene with triiron dodecacarbonyl. An X-ray study led to the suggestion that part of the bonding of the hydrocarbon system to an iron atom could be described in terms of a π -allylic bond (39), although the molecule did not contain a discrete π -allyltricarboxyliron moiety.

The first report of dimeric π -allyltricarboxyliron, which possessed an iron-iron bond, appeared in 1964 (40).

The reductive dehalogenation of π -allyltricarbonyliron halides by $\text{Na}^+\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)^-$ or $\text{Na}^+\text{Mn}(\text{CO})_5^-$ afforded bis(π -allyltricarbonyliron), which was in equilibrium in solution with the paramagnetic π -allyltricarbonyliron radical. A better route for the preparation of this compound was to chromatograph the halides on deactivated alumina.

Recently, several tricarbonyliron derivatives containing π -allylic system have been reported. These are a cyclooctatetraene derivative (41), a 1,3,5,7-tetramethylcyclooctatetraene derivative (42), an acenaphthylene derivative (43), and allene derivatives (44,45). The latter three types contain iron-iron bonds and their structures have been elucidated by a combination of NMR and infrared spectral techniques, and X-ray crystallography (46,47).

4. Theoretical aspect of the bonding in π -allyl metal compounds.

X-ray structural analyses (48,49,50,51) have shown that in π -allylpalladium chloride and acetate, the plane of the three allylic carbon atoms is not perpendicular to the plane of the $(\text{PdCl})_2$ bridge system. It is in fact oriented so that the central carbon atom, although actually closest to Pd, is tipped away from the metal; the terminal carbons are virtually equivalent (Figure 1).

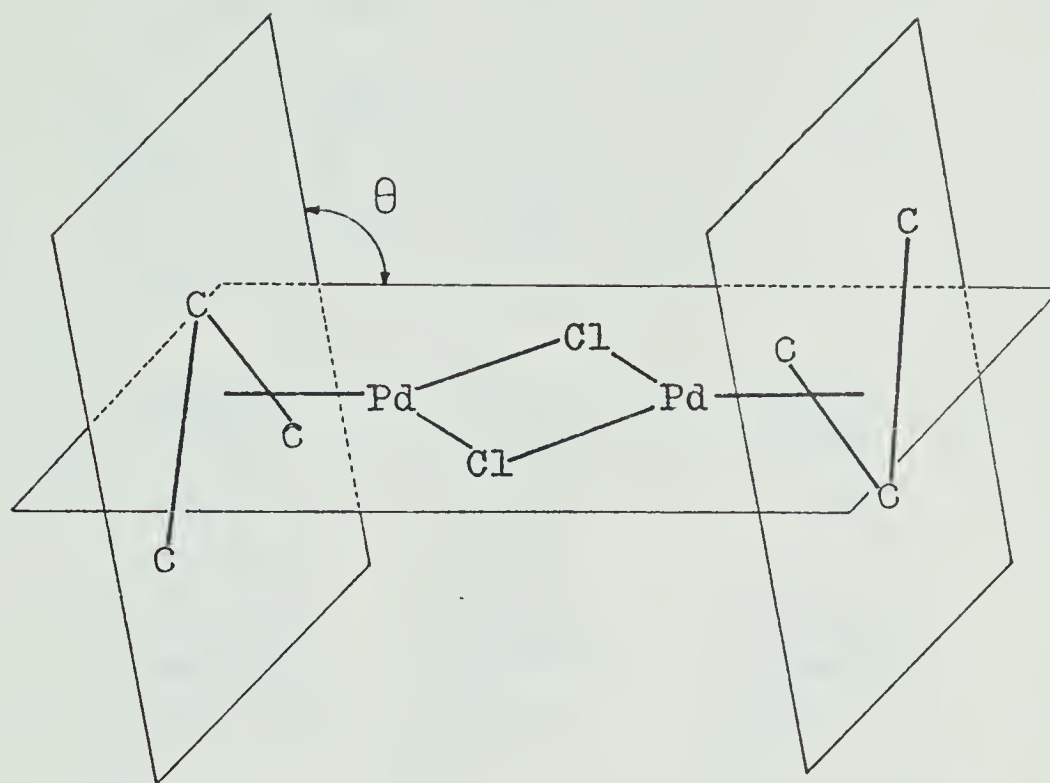


Figure 1 The structure of π -allylpalladium chloride dimer. Hydrogen atoms are not shown for simplicity. The dihedral angle is θ .

In π -allyltricarbonyliron iodide, the same structure of the π -allyl group has been observed (52).

The π -allyl group belongs to the C_{2v} point group, and the set of three p_{π} orbitals transforms as $A_2 + 2B_1$ irreducible representations. Molecular orbitals corresponding to these representations are shown in Figure 2, together with metal orbitals of suitable symmetry for bonding with them. From a simple LCAO-MO energy calculation, molecular orbitals belonging to the representations A_2 and $2B_1$ of C_{2v} can be expressed as follows:

$$\Phi_{B_1(1)} = \frac{1}{2}(\phi_1 + \sqrt{2}\phi_2 + \phi_3)$$

$$\Phi_{A_2} = \frac{1}{\sqrt{2}}(\phi_1 - \phi_3)$$

$$\Phi_{B_1(2)} = \frac{1}{2}(\phi_1 - \sqrt{2}\phi_2 + \phi_3)$$

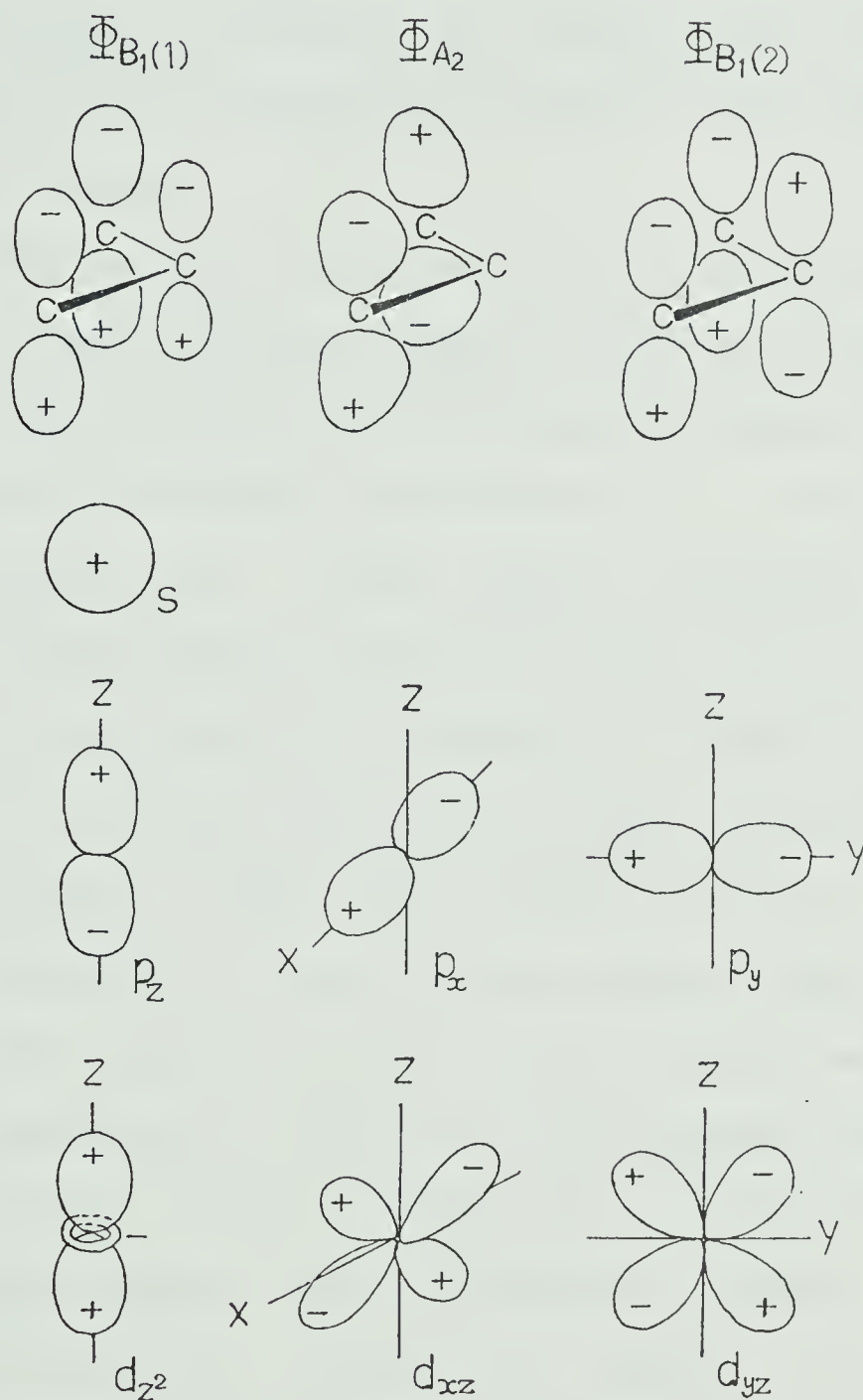


Figure 2. π -Allyl molecular orbitals and metal atomic orbitals for dihedral angle of 90° .

The extent of the interaction between the allyl and the metal orbitals will depend upon the overlap integral and upon the energy difference between the interacting orbitals. An estimation of the overlap integrals suggests that the strong bond seems to arise from the interactions between $\phi_{B_1(1)}$ and d_{z^2} , and between ϕ_{A_2} and d_{xz} (53). Thus the allyl group may be considered to bond to the metal by a σ -bond and π -bond.

It has, however, been pointed out by Kettle and Mason (53) that a dihedral angle of 90° is to be expected, if the bonding between the allyl group and the metal were analogous to that usually postulated for π -ethylene-platinum system (54). These authors discussed two limiting cases by which bonding between an allyl group and a metal can occur. One involved a geometry in which the dihedral angle is 90° (as shown in Figure 2) and the other involved a dihedral angle of 180° (the π -allyl plane is co-planar with the metal atom in the latter case as shown in Figure 3). The total bonding energy of the π -allyl-metal bond was then expressed as the sum of the bonding energies of the two distinct overlap mechanisms. By maximising the total bonding energy, they evaluated the optimum dihedral angles for the $\phi_{B_1(1)} - d_{z^2}$, d_{yz} , and $\phi_{A_2} - d_{xz}$, d_{xz} interactions as 114° and 102° , respectively, for π -allyl-palladium chloride. These values may be compared with the experimental values of 125° , 110° (51) and 108° (49).

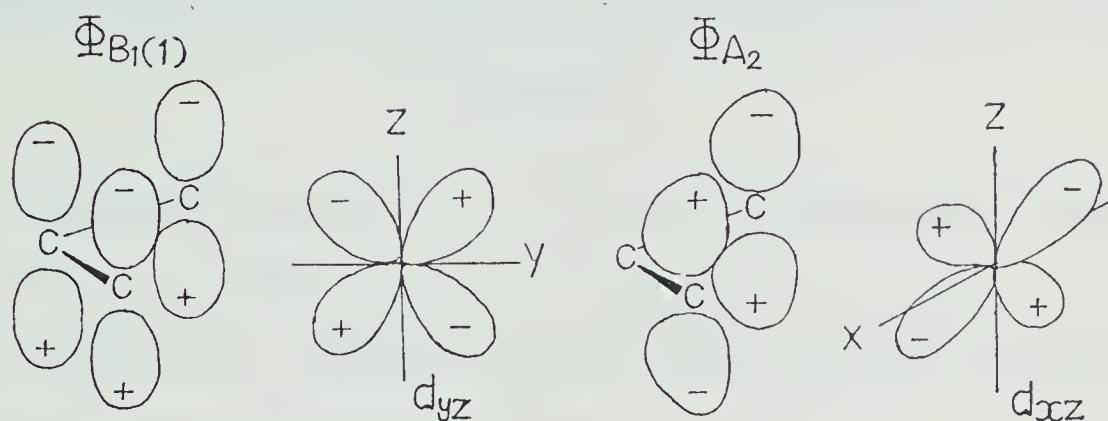


Figure 3. The molecular orbital scheme for the bonding of the π -allyl-metal system for dihedral angle of 180° .

From a rough estimate of the relative energies of the π -orbitals of the allyl system and d-orbitals of palladium based on their ionization potentials, it was concluded that the $\Phi_{B_1}(1)$ orbital plays the major role in the π -allyl-palladium bonding.

CHAPTER II

Synthesis of π -Allyltricarbonyliron Derivatives of Group IV Elements

Although numerous π -allyltricarbonyliron derivatives were known as detailed in the preceding Chapter, no previous attempt had been made to prepare derivatives of Group IV elements. It was with this end in view that a detailed synthetic study of a series of π -allyltricarbonyliron derivatives of Group IV elements was undertaken. After the commencement of the present work, one unsuccessful attempt was reported by Gubin and Denisovich (55).

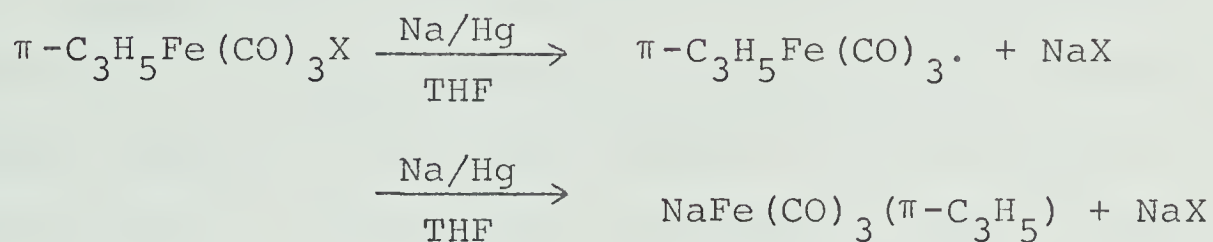
RESULTS AND DISCUSSION

1. General procedures

Many π -allyltricarbonyliron derivatives of Group IV elements discussed in this Chapter were prepared by displacement of halide ion from an organometallic halide by π -allyltricarbonyliron anion, $\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)^-$. After the discovery of the new anion in the present work, the anion was reported (56), and its properties were studied polarographically (55).

The anion was conveniently prepared in the present work by the reduction of $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{X}$ (where $\text{X} = \text{Cl}, \text{Br}, \text{I}$) using 1% sodium amalgam. A solution of $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{X}$ in THF was stirred with excess 1% sodium amalgam for about

60 minutes at room temperature. At the end of this period the solution had lost its original color and became pale green or sometimes gray due to suspended mercury.



The reduction of π -allyltricarbonyliron halide proceeds via the initial formation of the radical, $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3\cdot$, which further reacts with sodium to produce the 18-electron anion, $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3^-$, as shown by the Russian workers (55). These two one-electron reductions were demonstrated by polarographic studies and it was suggested that the initial step was irreversible, and that the second step was reversible from the electrochemical point of view. Electrochemical reversibility requires that the cathodic half-wave potential for reduction of the radical to the anion be equal to the anodic half-wave potential in the oxidation of the anion to the radical (55).

The infrared spectrum of $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3^-$ exhibited two broad bands at 1912 and 1860 cm^{-1} in the carbonyl stretching region in THF, in reasonable agreement with the reported values (55).

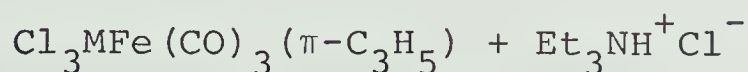
The preparation of $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3^-$, and its subsequent reactions, were always carried out in a nitrogen atmosphere

because of the rapidity with which the anion undergoes atmospheric oxidation.

Reaction of the anion with an organometallic halide was carried out by mixing solutions of stoichiometric quantities of anion (normally 10 mmoles were employed) and halide together in the same solvent, and stirring at room temperature or above until the bands at 1912 and 1860 cm^{-1} had disappeared to ensure that the reaction was complete. The reaction mixture was worked up by evaporating the solvent at room temperature or below under reduced pressure using a rotary evaporator. The residue from this evaporation was then extracted with n-pentane, and the extract filtered and evaporated under reduced pressure to a small volume, or until crystals began to form. The solution was then cooled either to about -20° or -80° to complete crystallization. The product was then usually recrystallized from n-pentane. In the work-up of reaction mixtures containing a volatile product (trimethyltin, trimethylgermanium, and perfluorocarbon derivatives), solvent was first removed at 0° in vacuo, and the product was obtained by sublimation of the residue onto a -78° probe. When greater purity was required, the sublimate was purified by an additional sublimation under high vacuum or by recrystallization from n-pentane.

Trichlorosilicon and trichlorogermanium derivatives were prepared by the reactions of π -allyltricarboxyliron

chloride with HSiCl_3 or HGeCl_3 in the presence of triethylamine in hydrocarbon solvent, e.g.,



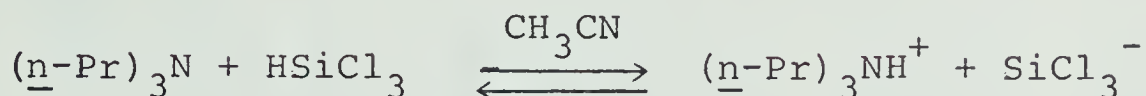
(M = Si, Ge)

The progress of the reaction could be followed by infrared measurements of the reaction mixture in the carbonyl stretching region. Usually after 5 - 6 hours, the starting material had completely disappeared and three new carbonyl stretching bands appeared. The reaction mixture was then worked up as described above.

The mechanism of this reaction is not entirely clear. In the case of trichlorogermane, similar reaction has been classified as an insertion reaction of GeCl_2 into a metal-chlorine bond, because it is known HGeCl_3 can serve as a source of GeCl_2 (57). In the present case, the reaction may perhaps proceed via interaction of HGeCl_3 with triethylamine giving the unstable carbenoid, GeCl_2 , which may then insert into the iron-chlorine bond as usually postulated in the insertion reactions.

On the other hand, Benkeser et al. (58), in a recent study of the HSiCl_3 -amine system in acetonitrile, have shown that the trichlorosilyl anion, SiCl_3^- , is

present, and that the following equilibrium lies far to the right:



This ion could well be the reactive species in the formation of trichlorosilylmetal derivatives, using the technique involving amines. It is also possible that a mechanism of this type may operate with trichlorogermane, rather than the GeCl_2 insertion reaction mentioned above.

It may be noteworthy here that Ph_3MH , (where $\text{M} = \text{Si}, \text{Ge}$), did not react with π -allyltricarbonyliron chloride under the same or more rigorous conditions.

2. Synthesis of germanium derivatives

Compounds with one or two π -allyltricarbonyliron groups bonded to germanium were prepared, their analytical data, colors and melting points being given in Table I. Spectroscopic studies are described in detail in Chapter III.

Germanium derivatives were usually prepared by halide displacement reactions involving treatment of equimolar quantities of an organogermanium halide with $\text{NaFe}(\text{CO})_3^-(\pi\text{-C}_3\text{H}_5)$ in THF solution:

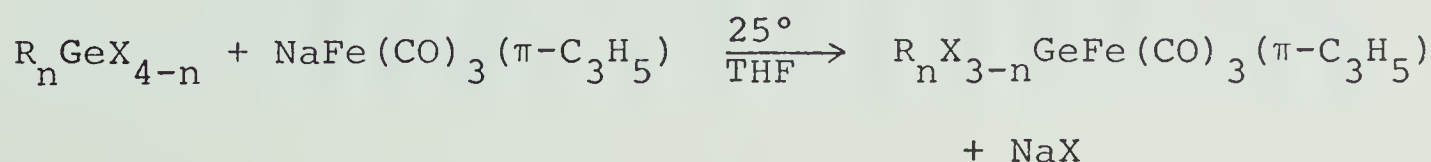


TABLE I

Analytical Data, Colors and Melting Points for Silicon, Germanium, Lead and Fluorocarbon Derivatives

Compound	M.P. (°C)	Color	Calcd %				Found %			
			C	H	X		C	H	X	
$\text{Cl}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	136-137	Yellow	20.02	1.04	29.55		20.22	1.69		29.65
$\text{PhCl}_2\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	98-100	Yellow	35.89	2.57	17.66		35.94	2.48		17.71
$\text{MeCl}_2\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	64-65	Yellow	24.77	2.38	20.89		24.97	2.41		20.89
$\text{Ph}_2\text{ClGeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	99-101	Pale Yellow	48.78	3.41	8.00		48.88	3.41		7.96
$\text{Me}_2\text{ClGeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	44-46	Pale Yellow	30.12	3.48	11.11		29.75	3.39		11.20
$\text{Br}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	dec.136	Orange	14.61	1.02	48.60		14.63	1.22		48.60
$\text{Ph}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	109-111	Pale Yellow	59.58	4.16	-		59.44	3.99		-
$\text{Me}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	Liquid	Pale Yellow	36.20	4.73	-		-	-		-
$\text{Br}_2\text{Ge}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	dec.135	Orange	24.25	1.70	26.89		24.11	1.57		26.72
$\text{Cl}_3\text{SiFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	91	Yellow	22.85	1.60	33.72		22.91	1.76		33.70
$\text{CF}_3\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	Liquid	Pale Yellow	33.64	2.02	-		-	-		-
$\text{C}_3\text{F}_7\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	Liquid	Pale Yellow	30.89	1.44	-		31.70	1.88		-
$\text{Ph}_3\text{PbFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	79	Brown	46.54	3.25	-		46.48	3.48		-
$\text{Ph}_2\text{Pb}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	89	Red	39.85	2.79	-		39.76	2.82		-

where

$n = 0,$	$X = \text{Br}$
$n = 1,$	$X = \text{Cl}, R = \text{Me}, \text{Ph}$
$n = 2,$	$X = \text{Cl}, R = \text{Me}, \text{Ph}$
$n = 3,$	$R = \text{Me}, \text{Ph}$

The trichlorogermanium derivative was, however, prepared by the reaction between π -allyltricarbyliron chloride and HGeCl_3 as mentioned in the preceding section. The displacement reaction was complete in 60 minutes, and the reaction mixture was worked up by the evaporation of solvent and extraction of the residue with n-pentane. Evaporation of the extract to a small volume followed by cooling afforded crystals of product. All the derivatives prepared formed pale-yellow to orange crystals, soluble in both polar and nonpolar solvents. All are air-stable in the solid state except $\text{Me}_3\text{GeFe}(\text{CO})_3 (\pi\text{-C}_3\text{H}_5)$, but are oxidized in a few hours in solutions exposed to air. They also possess moderate thermal stability, decomposing only above about 100° .

Attempts to replace more than one halide ion by treatment of $\text{R}_n\text{GeX}_{4-n}$ (where $n = 1, 2$) with two ($n = 2$) and three ($n = 1$) fold quantities of $\text{NaFe}(\text{CO})_3 (\pi\text{-C}_3\text{H}_5)$ did not succeed. This is surprising considering that bis(π -allyltricarbyliron)germanium dibromide could be obtained by the reaction between the anion and GeBr_4 , although it was

not a major product. Even under more rigorous conditions (50°, 10 hours), the reaction mixture did not show evidence for the formation of the bis-substituted derivative. This was confirmed by means of infrared measurements of the reaction mixture. This may be partly due to the decrease in polarity of the Ge-X bond owing to alkyl substituents on germanium atom, and partly due to the steric factor which involves the difficulty in bringing the second $\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)^-$ group close enough to germanium to react.

3. Synthesis of tin derivatives

Tin derivatives prepared in this work are listed in Table II, together with analytical data, colors and melting points. They were mostly prepared by halide displacement reactions. The reaction of triphenyltin chloride with $\text{NaFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ requires comment. This reaction has been recently reported by Gubin and Denisovich (55), and the only product isolated was hexaphenylditin. However, in the present work the reaction was performed at 40 - 50° for about 5 hours and the anticipated triphenyl(π -allyltricarboxyliron)tin(IV), $\text{Ph}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, could be obtained.

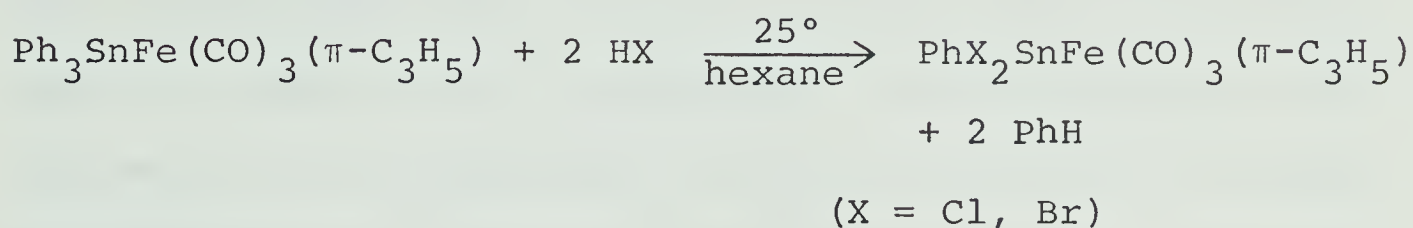
Reactions of organotin di- and trihalides with equimolar quantities of $\text{NaFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ gave only bis(π -allyltricarboxyliron) derivatives. By means of the halide displacement reaction, it was impossible to prepare mono-

TABLE II

Analytical Data, Colors and Melting Points for Tin Derivatives

Compound	M.P. (°C)	Color	Calcd %			Found %		
			C	H	X	C	H	X
$\text{Cl}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	Dec.104	Orange	17.66	1.24	26.07	17.60	1.27	26.19
$\text{Br}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	Dec.91	Orange	13.31	0.93	44.28	13.23	0.93	44.42
$\text{PhCl}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	69-70	Yellow	32.20	2.25	15.84	31.82	2.19	15.66
$\text{PhBr}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	68-69	Yellow	26.86	1.88	29.79	26.68	1.91	29.79
$\text{PhI}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	89-90	Orange	22.86	1.60	40.25	23.63	1.57	39.20
$\text{Ph}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	86	White	54.29	3.80	-	53.75	3.68	-
$\text{Me}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	Liquid	Pale Yellow	31.36	4.09	-	28.53	4.06	-
$\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	88-90	Orange	27.64	1.93	13.60	26.58	1.90	13.72
$\text{I}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	Dec.105	Red	20.46	1.43	36.03	20.40	1.24	36.01
$\text{PhClSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	105-107	Orange	36.45	2.55	5.98	36.40	2.85	6.00
$\text{PhBrSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	109-110	Orange	33.91	2.37	12.53	33.78	2.41	12.60
$\text{MeClSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	68-70	Orange	29.02	2.44	6.59	29.34	2.39	6.83
$\text{MeBrSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	70-71	Orange	27.13	2.28	13.88	27.28	2.34	14.20
$\text{Ph}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	132-133	Pale Yellow	45.41	3.18	-	45.13	3.28	-

or tris(π -allyltricarbonyliron) derivatives. Monosubstituted derivatives, therefore, were prepared by the reaction of $\text{Ph}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ with hydrogen halides, e.g.,



The iodo-derivatives, $\text{PhI}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ and $\text{I}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$ were prepared from the corresponding chloro-derivatives by treatment with sodium iodide in acetone solution.

The compounds formed pale-yellow to red crystals and were air-stable for long periods, except $\text{Me}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, which melted below room temperature to a very air-sensitive liquid.

Attempts to prepare $\text{Ph}_2\text{XSnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ by cleavage with HX under varying reaction conditions or by altering the ratio of reagents did not succeed. However, cleavage of one phenyl group was observed in the infrared spectrum at an early stage of the reaction. When $\text{Ph}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ in hexane was treated with an equimolar amount of hydrogen chloride in THF at room temperature with vigorous stirring, about one-tenth of the starting material was converted into $\text{Ph}_2\text{ClSnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ within 30 minutes with no trace of $\text{PhCl}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, as judged from the infrared spectrum of the reaction mixture. After about half of the starting

material had reacted with hydrogen chloride, the infrared spectrum of the reaction mixture provided evidence of the presence of $\text{PhCl}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$; an approximate mole ratio of $\text{Ph}_2\text{ClSnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ and $\text{PhCl}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ was 1:5, based on band intensities. It was observed that the amount of $\text{PhCl}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ continued to increase as compared with that of $\text{Ph}_2\text{ClSnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$. This may be due to the increased polarity of the covalent bond, $\delta^- \delta^+$ C—Sn, in $\text{Ph}_2\text{ClSnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, which would make scission of the C—Sn bond easier; therefore $\text{Cl}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ would be produced smoothly in this way.

Under the conditions investigated, the Sn—Fe bond was preserved in the above reaction, whereas the Sn—Fe bond was cleaved when $\text{Me}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ was hydrochlorinated under the same conditions. Similarly, $\text{Ph}_3\text{PbFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ gave cleavage products of the Pb—Fe bond with hydrogen chloride.

EXPERIMENTAL

Melting points were determined by use of a Gallenkamp melting-point apparatus and a Kofler hot stage. All values are uncorrected. Microanalyses were performed by Mrs. Darlene Mahlow of the University of Alberta Chemistry Department Microanalytical Laboratory.

All reactions and subsequent operations were carried out under a static nitrogen atmosphere maintained at a

slight positive pressure by a paraffin oil bubbler. All products were handled with minimum exposure to air.

Solvents: Tetrahydrofuran (THF) was distilled over LiAlH_4 to remove moisture and traces of peroxide. In every other case reagent grade solvents were used without further purification.

Reagents: Sodium amalgam - Mercury (13 ml., ca. 175 g.) was placed in a one-neck 250 ml. flask fitted with a side-arm and stopcock. The flask was tilted so that the side-arm was above the level of the mercury. The mercury was stirred with a magnetic stirrer and nitrogen blown over it via the side-arm. Sodium metal (2.5 g.) was cut into small pieces under n-pentane and carefully added to the mercury. When all the sodium had been added, the amalgam was allowed to cool to room temperature, and the reduction of π -allyltricarboxyliron halide carried out in the same apparatus.

Diiron enneacarbonyl, $\text{Fe}_2(\text{CO})_9$. This was prepared by the procedure described by King (59). A mixture of 30 ml. (44 g.) of iron pentacarbonyl and 220 ml. of glacial acetic acid was charged into a cylindrical quartz vessel cooled by running water. It was irradiated several hours by using Hanovia Type 679A36 450 watt medium pressure mercury lamp. As the irradiation proceeded, yellow fluffy

crystals of diiron enneacarbonyl separated from the reaction mixture. These were filtered, washed with ethanol and dried in vacuo. Five hours irradiation usually gave a 40 - 50% yield.

π -Allyltricarbonyliron bromide, $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3\text{Br}$. This was prepared by the method described by Murdoch and Weiss (35). To a suspension of $\text{Fe}_2(\text{CO})_9$ (18 g.) in 100 ml. of n-pentane, a three-fold excess of allyl bromide was added. It was then heated at refluxing temperature for 90 minutes with stirring. The resultant deep brown reaction mixture gave 12 g. of brown solid after the evaporation of volatiles by water-aspirator (20-30°/10-20 mm.). Extraction of the solid with 20 ml. of methylene chloride and filtration followed by evaporation of the solvent afforded 8.7 g. of brown crystals of product (67% yield, based on $\text{Fe}_2(\text{CO})_9$ employed).

π -Allyltricarbonyliron chloride, $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3\text{Cl}$, and π -allyltricarbonyliron iodide, $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3\text{I}$ were prepared similarly using allyl chloride or allyl iodide instead of allyl bromide. Typically, yields of $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3\text{Cl}$ and $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3\text{I}$ were 20-30 and 70-90% respectively, based on $\text{Fe}_2(\text{CO})_9$ used.

In every other case, reagents were obtained from commercial sources.

Preparation of π -allyltricarboxyliron derivatives.

The majority of these compounds were prepared by halide displacement using $\text{NaFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ in THF. Table III lists conditions used, together with the yields obtained. The preparations of triphenyl(π -allyltricarboxyliron)tin(IV), $\text{Ph}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, trimethyl(π -allyltricarboxyliron)tin(IV), $\text{Me}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, and trichloro(π -allyltricarboxyliron)tin(IV), $\text{Cl}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ are described as representatives of halide displacement reactions.

Triphenyl(π -allyltricarboxyliron)tin(IV), $\text{Ph}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$: Triphenyltin chloride (3.8 g., 10 mmoles) in 10 ml. of THF was treated with 10 mmoles of $\text{NaFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ in 150 ml. of the same solvent at 40-50° for 5 hours with stirring. The color changed from greenish gray to grayish brown. THF was removed from the reaction mixture under reduced pressure. Extraction of the dark brownish residue with 200 ml. of n-pentane, followed by concentration to about 50 ml. and cooling to -80°, afforded pale yellow crystals of product. This was recrystallized twice from n-pentane to give 3.7 g. of analytically pure crystals (70% yield).

Trimethyl(π -allyltricarboxyliron)tin(IV), $\text{Me}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$: Trimethyltin chloride (2.0 g., 10 mmoles) in 5 ml. of THF was treated with 10 mmoles of $\text{NaFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ in 150 ml. of the same solvent at room temperature for one hour with stirring. No particular color change was observed.

TABLE III

Experimental Data for the Preparation of π -Allyltricarboonyliron Derivatives of

Group IV Elements						
Compound	Carbonyl ^a	Reagent/Solv. ^b	Method ^c	Temperature (°C)	Time (hr)	Yield %
$\text{CF}_3\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	A	$\text{CF}_3\text{COCl/THF}$	HD	25	2	25
$\text{C}_3\text{F}_7\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	A	$\text{C}_3\text{F}_7\text{COCl/THF}$	HD	45	20	57
$\text{Cl}_3\text{SiFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	B	$\text{HSiCl}_3/\text{hex.}$	HA	R.T.	5	41
$\text{Cl}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	B	$\text{HGeCl}_3/\text{hex.}$	HA	R.T.	6	14
$\text{PhCl}_2\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	A	$\text{PhGeCl}_3/\text{THF}$	HD	R.T.	1	35
$\text{Ph}_2\text{ClGeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	A	$\text{Ph}_2\text{GeCl}_2/\text{THF}$	HD	R.T.	1	43
$\text{MeCl}_2\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	A	$\text{MeGeCl}_3/\text{THF}$	HD	R.T.	1	52
$\text{Me}_2\text{ClGeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	A	$\text{Me}_2\text{GeCl}_2/\text{THF}$	HD	R.T.	1	56
$\text{Br}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	A	$\text{Br}_4\text{Ge/THF}$	HD	R.T.	10	15
$\text{Br}_2\text{Ge}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	A	$\text{Br}_4\text{Ge/THF}$	HD	R.T.	10	5
$\text{Ph}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	A	$\text{Ph}_3\text{GeCl/THF}$	HD	R.T.	1	75
$\text{Me}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	A	$\text{Me}_3\text{GeBr/THF}$	HD	R.T.	1	15
$\text{Cl}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	A	$\text{Cl}_4\text{Sn/THF}$	HD	R.T.	10	15
B		$\text{Cl}_2\text{Sn/benz.}$	IR	60-70	10	25

(continued)

TABLE III (continued)

Compound	Carbonyl ^a	Reagent/Solv ^b	Method ^c	Temperature (°C)	Time (hr)	Yield %
$\text{Br}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	A	$\text{Br}_4\text{Sn}/\text{THF}$	HD	R.T.	15	15
	C	$\text{Br}_2\text{Sn}/\text{benz.}$	IR	60-70	10	15
$\text{PhCl}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	D	$\text{HCl}(\text{gas})/\text{hex.}$	HF	R.T.	0.1	95
$\text{PhBr}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	D	Br_2/CCl_4	HF	R.T.	3	40
$\text{PhI}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_4\text{H}_5)$	E	KI/acetone	MR	R.T.	2	21
$\text{Ph}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	A	$\text{Ph}_3\text{SnCl}/\text{THF}$	HD	40-50	5	70
$\text{Me}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	A	$\text{Me}_3\text{SnCl}/\text{THF}$	HD	R.T.	1	15
$\text{Ph}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	A	$\text{Ph}_2\text{SnCl}_2/\text{THF}$	HD	45	5	63
$\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	F	HCl/THF	HF	R.T.	2	97
$\text{PhClSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	A	$\text{PhSnCl}_3/\text{THF}$	HD	R.T.	1	65
$\text{PhBrSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	G	KBr/THF	MR	R.T.	3	40
$\text{MeClSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	A	$\text{MeSnCl}_3/\text{THF}$	HD	R.T.	1	42
$\text{MeBrSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	H	KBr/THF	MR	R.T.	3	15
$\text{I}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	I	KI/acetone	MR	R.T.	1	47
$\text{Ph}_3\text{PbFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	A	$\text{Ph}_3\text{PbCl}/\text{THF}$	HD	R.T.	1	60
$\text{Ph}_2\text{Pb}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	A	$\text{Ph}_2\text{PbCl}_2/\text{THF}$	HD	R.T.	1	20

(continued)

FOOTNOTES TO TABLE III

- a $A = \text{NaFe}(\text{CO})_3(\text{C}_3\text{H}_5)$, $B = \pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Cl}$, $C = \pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Br}$, $D = \text{Ph}_3\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$, $E = \text{PhCl}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, $F = \text{Ph}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$, $G = \text{PhClSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$, $H = \text{MeClSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$, $I = \text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$
- b hex. = hexane, benz. = benzene.
- c HD = halide displacement reaction, HA = hydrogen chloride abstraction reaction by triethylamine, IR = insertion reaction, HF = fission reaction by hydrogen halide or halogen, MR = metathetical reaction with potassium halide. All refer to the methods described in the experimental section of Chapter II.
-

After removal of THF in vacuo at 0°, the residue was extracted with 50 ml. of n-pentane. The n-pentane extract was shaken with 30 ml. of 5% aqueous KF solution for 15 minutes to convert unreacted trimethyltin chloride to the insoluble fluoride (60). The n-pentane layer was collected and n-pentane was removed in vacuo. The resultant brownish residue was purified by sublimation at room temperature onto a -78° probe. The sublimate was a red, oily solid, which was dissolved in 10 ml. of n-pentane, followed by cooling to -80° to give pale-yellow crystals of product (final yield 0.5 g., 15%).

The red color originates from bis(π -allyltricarboxyl-iron). Difficulty was encountered in separating the product from it.

Trichloro(π -allyltricarboxyliron)tin(IV), $\text{Cl}_3\text{SnFe}(\text{CO})_3-$
 $(\pi\text{-C}_3\text{H}_5)$: Tin tetrachloride (2.3 g., 10 mmoles) was added to a THF solution of $\text{NaFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ (10 mmoles) and stirred at room temperature for 12 hours. The resultant deep-red reaction mixture was worked up as mentioned previously, the product being a mixture of $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Cl}$ and $\text{Cl}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$. The latter could be separated in an analytically pure state by recrystallization from n-pentane (yield, 0.6 g., 15%). Similarly, $\text{Br}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ was prepared by using tin tetrabromide.

These compounds could, however, be better prepared by

insertion reactions. In a typical insertion reaction, 10 mmoles of $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{X}$ (where $\text{X} = \text{Cl}, \text{Br}$) were dissolved in 100 ml. of benzene and 10 mmoles of SnX_2 were added. The mixture was stirred for about 10 hours at $60\text{--}70^\circ$. The solvent was removed and the red, oily residue was extracted with a minimum amount of methylene chloride. Addition of n-pentane, followed by cooling to -20° , afforded orange crystals of product. Usually, yields of 20-40% were obtained. The latter method appeared to be superior to the former. Attempts to prepare the corresponding iodo-derivative by insertion of SnI_2 were unsuccessful.

In contrast to SnCl_2 and SnBr_2 , PbCl_2 and PbBr_2 did not appear to be at all reactive towards $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{X}$.

Trichloro(π -allyltricarboxyliron) silicon(IV), $\text{Cl}_3\text{Si-Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, and Trichloro(π -allyltricarboxyliron)-germanium(IV), $\text{Cl}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$: Trichlorosilane (4.0 g., 30 mmoles) and 2.1 g. (10 mmoles) of $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Cl}$ were dissolved in 100 ml. of hexane, to which 1.0 g. (10 mmoles) of triethylamine was then added. The progress of the reaction was followed by infrared measurements. After about 5 - 6 hours stirring at room temperature, the infrared spectrum of the reaction mixture showed three new bands and no evidence for the presence of $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Cl}$. The reaction mixture was then worked up as described previously. A yield of 41% was obtained.

Similarly, $\text{Cl}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ was obtained in 14% yield.

Dihalophenyl(π -allyltricarboxyliron)tin(IV), $\text{PhX}_2\text{Sn-Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$: These derivatives were prepared by the reactions of $\text{Ph}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ with hydrogen halides.

Typically, 2.65 g. (5 mmoles) of $\text{Ph}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ was dissolved in 100 ml. of hexane, and hydrogen chloride was then slowly introduced (2-3 bubbles per sec.). The progress of the reaction was followed by infrared measurements of the reaction mixture in the carbonyl stretching region, stopping the introduction of the gas intermittently. After the gas had been passed into the solution for a total of about 5 minutes, the starting material had completely disappeared and the infrared spectrum of the reaction mixture exhibited three unsymmetrical doublets in the carbonyl stretching region. The solvent was then removed from the reaction mixture under reduced pressure, to afford yellow crystals of product. This was recrystallized from n-pentane (2.2 g., quantitative yield).

Similarly, $\text{PhBr}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ was prepared in 25% yield using hydrogen bromide. The latter could be also prepared by the reaction between $\text{Ph}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ and bromine. To a hexane solution of $\text{Ph}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ (2.65 g., 5 mmoles), 3.2 g. (20 mmoles) of bromine in 25 ml. of carbon tetrachloride was added from a dropping funnel over a period of one hour, and the solution was stirred

for an additional 2 hours. The reaction mixture was then worked up as described above. A yield of 40% of $\text{PhBr}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ was obtained. Both methods described here for the preparation of $\text{PhBr}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ gave minor yields of $\text{Br}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ as well; the latter could be separated from the main product by recrystallization from a methylene chloride - pentane mixture.

Diiodophenyl(π -allyltricarboxyliron)tin(IV), $\text{PhI}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, and Diiodobis(π -allyltricarboxyliron)tin(IV), $\text{I}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$: These compounds were prepared from the corresponding chloro-derivatives by treatment with sodium iodide in acetone solution. Typically, 1.0 mmole of $\text{PhCl}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ or $\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$ was dissolved in acetone, and 2.0 mmoles of sodium iodide, dissolved in the same solvent, was added with stirring at room temperature. Sodium chloride precipitated, and the reaction mixture turned orange. The acetone was removed under reduced pressure and the residue was extracted with n-pentane. Concentration to a small volume, followed by cooling to -20° afforded crystals of product. A yield of 20-50% of product was obtained, after recrystallization from n-pentane at -20° .

Trifluoromethyl- π -allyltricarboxyliron, $\text{CF}_3\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$: To a solution of $\text{NaFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ (10 mmoles)

in 150 ml. of THF, CF_3COCl was introduced directly as a gas from the metal container in which it was supplied. Bubbling was adjusted using a needle valve to 2-3 bubbles per second. After 2 hours at room temperature, the gas was stopped and volatiles were removed from the reaction mixture in vacuo at 0° . The product was obtained by sublimation of the residue onto a -78° probe. A red oil was first sublimed and discarded. A pale yellow solid was obtained by further sublimation. This was purified by an additional sublimation to give about 0.5 g. of product ($\sim 25\%$ yield, based on the anion used).

Similarly, heptafluoro-n-propyl- π -allyltricarbonyliron, $\sigma\text{-C}_3\text{F}_7\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ could be obtained by treatment of $\text{NaFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ with a stoichiometric amount of n- $\text{C}_3\text{F}_7\text{COCl}$ (1.7 g., 55% yield). Both derivatives exhibited only terminal carbonyl stretching bands in their infrared spectra.

Reaction of Me_2SnCl_2 with $\text{NaFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$: In an attempt to prepare $\text{Me}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$, a solution of 1.1 g. (5 mmoles) of Me_2SnCl_2 in 10 ml. of THF was stirred at room temperature and a solution of 10 mmoles of $\text{NaFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ in 150 ml. of the same solvent was added. After stirring for 60 minutes, the THF was removed under reduced pressure and the residue was extracted with n-pentane. By evaporation of the extract, 0.2 g. of orange powder was obtained. The infrared spectrum of the latter in the carbonyl stretching region was somewhat similar to that of

$\text{Ph}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$. However, the reaction was found to be more complex than expected, and was not reproducible. Different products were obtained in subsequent experiments.

Attempts were then made to obtain the product by sublimation. After the THF was removed from the reaction mixture, red, air-sensitive oil sublimed from the residue onto a -78° probe. The latter was characterized as bis(π -allyltricarboxyliron), based on its infrared spectrum. A similar phenomenon was also encountered when MeSnCl_3 or Me_3SnCl was treated with $\text{NaFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$.

Reaction of Ph_3SiCl with $\text{NaFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$: In an attempt to prepare a triphenylsilyl derivative, a solution of 3.2 g. (10 mmoles) of Ph_3SiCl in 100 ml. of THF was treated with an equimolar amount of $\text{NaFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ in 150 ml. of the same solvent at room temperature. After stirring for about one hour, the THF was removed under reduced pressure and the residue was first extracted with 200 ml. of n-pentane. The extract was filtered, concentrated and cooled to -80° to afford 0.4 g. of $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Cl}$. A further extraction of the residue with methylene chloride, followed by evaporation of the solvent gave only a small amount of Ph_6Si_2 , which was identified mass spectrometrically. The anticipated product was not obtainable in this way. The reaction seems somewhat similar to the unsuccessful attempt to react Ph_3SiCl with $\text{NaMn}(\text{CO})_5$ (61), and the

course of the reaction remains obscure. An alternative reaction between $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3\text{Cl}$ and LiSiPh_3 or Ph_3SiH in an appropriate solvent was also unsuccessful, only bis(π -allyltricarboxyliron) being isolated.

Reaction of PMe_2Ph with $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3\text{Br}$: A solution of 1.4 g. (10 mmoles) of PMe_2Ph and 1.3 g. (5 mmoles) of $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3\text{Br}$ in 50 ml. of benzene was heated at $70\text{--}80^\circ$ with stirring. After 12 hours, the benzene was removed under reduced pressure and the residue was extracted with 200 ml. of n-pentane in several portions. The combined n-pentane extract was concentrated to about 50 ml. and cooled to -20° in a freezer. Brown crystals came down and these were recrystallized from a methylene chloride-pentane mixture at -20° to afford 1.2 g. of deep-brown crystalline plates (m.p. 151°). However, these were not the anticipated product, and were characterized as the known $(\text{PhMe}_2\text{P})_2\text{Fe(CO)}_2\text{Br}_2$ (62) by elemental analysis.

Anal. Calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{Br}_2\text{P}_2\text{Fe}$: C, 39.39, H, 4.01, Br, 29.17. Found: C, 39.40, H, 4.04, Br, 28.69.

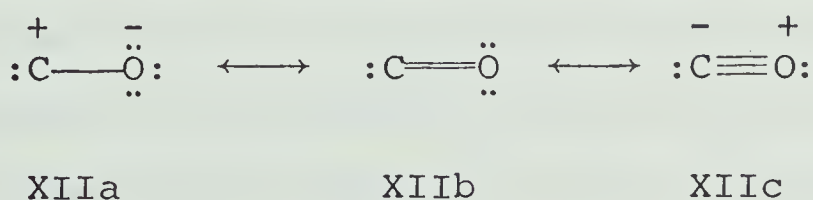
The proton NMR spectrum showed a triplet (in the CH_3 region) ($|J_{\text{AX}} + J_{\text{A,X}}| = 18.0$ cps) centered at τ 7.84 in CDCl_3 consistent with the proposed structure (62) in which the two phosphine groups are mutually trans and the two carbonyls are cis to each other. The infrared spectrum, however, exhibited two doublets in cyclohexane solution in

the carbonyl stretching region (2036, 2032 and 1984, 1980 cm^{-1}); these doublets were not resolved in a polar solvent such as CHCl_3 , where only two bands were observed. The occurrence of two doublets in cyclohexane could be attributed to the presence of conformational isomers analogous to those observed in $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_3\text{PMe}_2\text{Ph}$ (Chapter V, 5).

CHAPTER IIISpectroscopic StudiesA. Infrared Spectra in the Carbonyl Stretching RegionINTRODUCTION

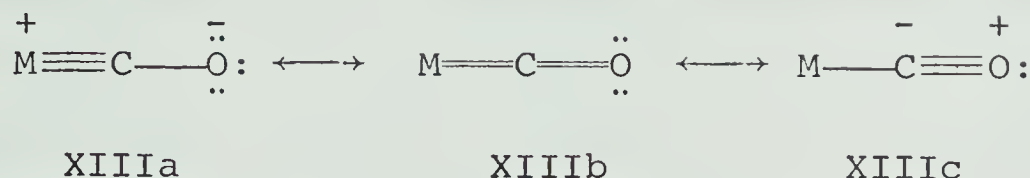
One of the important applications of carbonyl vibrational spectra is the elucidation of molecular structure. This can be done by the interpretation of the number of bands, the frequency range in which the bands are found, and to some extent their relative intensities. The number of bands depends upon the number of carbonyl groups as well as the symmetry of the whole molecule. The actual procedure used to predict the maximum number and symmetry of carbonyl stretching modes is found in many texts (63,64).

The carbonyl stretching frequencies of metal carbonyls decrease as the extent of nonbonding electron back-donation from the metal to the anti-bonding orbitals of carbonyl group increases. The back-donation causes an increase of the metal-carbon bond order and a decrease of the CO bond order by the same amount. Since carbon monoxide can be regarded as a resonance hybrid of XIIa - XIIc,



a terminal carbonyl group on a metal can be regarded as a

resonance hybrid of XIIIa - XIIIc:



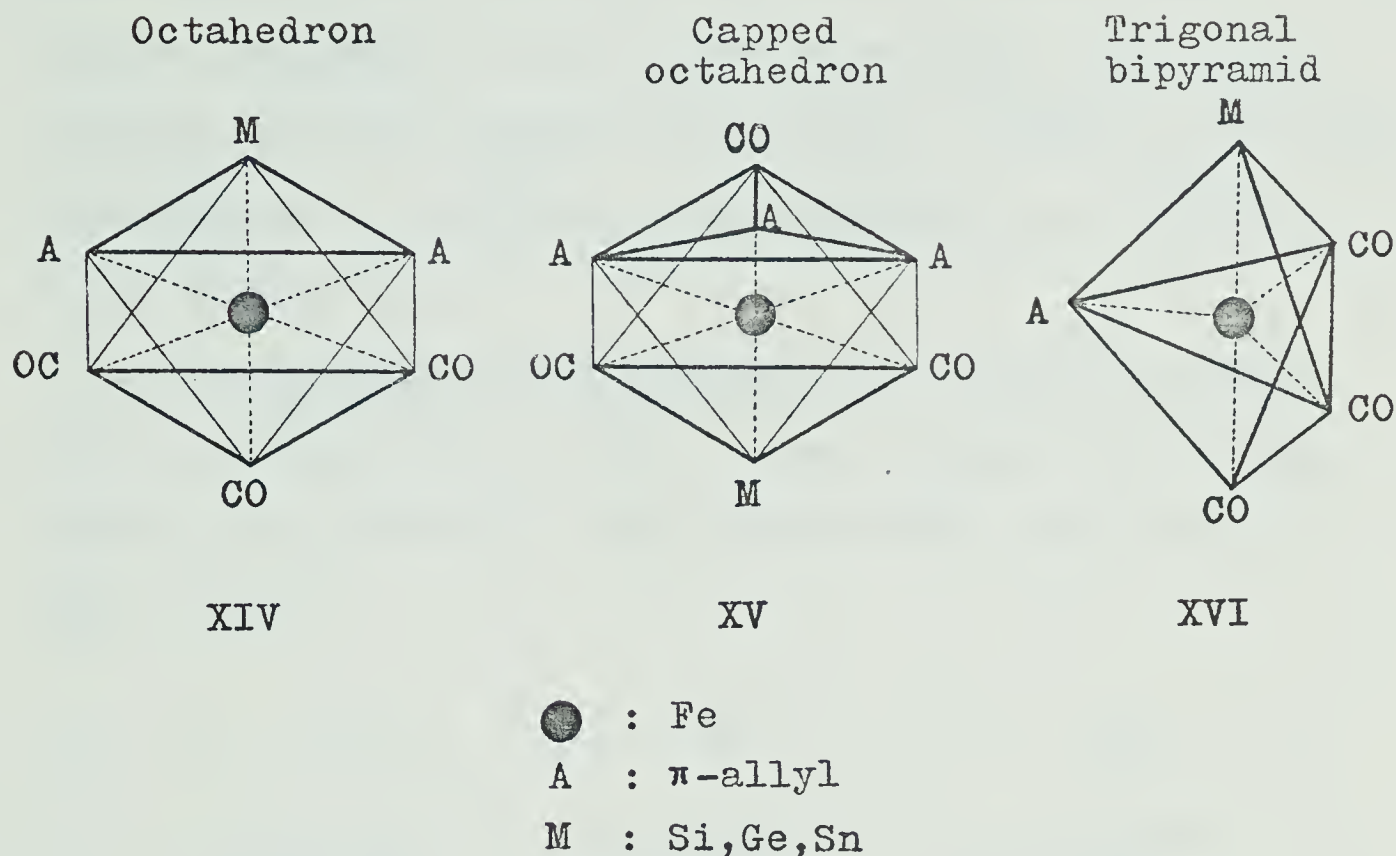
The total bond order of the M—C—O system is, therefore, regarded as four, and the accumulation of negative charge on the metal atom stimulates the back-donation to the carbonyl group, thus giving rise to multiple bond character of the M—C bond. This in turn causes a drop in the carbonyl stretching frequency (65). This is reflected in the observed stretching frequencies of metal carbonyls, for which values ranging from 2100 to 1800 cm^{-1} are usually observed, indicating a C—O bond order between two and three (carbon monoxide absorbs at 2143 cm^{-1} , whereas ketones absorb at ca. 1700 cm^{-1}). On the other hand, back-donation enables all carbonyl groups on the metal atom to interact with each other; that is, the vibration of one carbonyl group can affect the vibrations of the other carbonyl groups through the metal d-orbitals, and the vibrations are said to be coupled. Thus, the stretching of the CO bond from its equilibrium position stimulates back-donation from the filled metal d-orbitals to the anti-bonding orbital of the carbonyl group and vice versa. There is consequently competition for the metal d-electron density when all the carbonyl groups vibrate symmetrically

at the same time. It is generally believed that the vibration which involves the symmetric stretching of the greatest number of carbonyl groups will have the highest frequency. This principle is useful in the assignment of the observed bands to the possible modes of vibration.

Finally, it may be noted that since the intensity of an infrared absorption band is proportional to the square of the rate of change of dipole moment with respect to the displacement of the atoms, the relative intensities of carbonyl stretching bands are sometimes also helpful in the assignment.

RESULTS AND DISCUSSION

From a consideration of relative intensities of the carbonyl stretching bands of $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3\text{MR}_3$, together with the available crystal structure of $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3\text{I}$ in which all carbonyl groups are cis to each other (52), $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3\text{MR}_3$ can be conveniently regarded as having any of three idealized geometries. If one regards the π -allyl group as a bidentate ligand, the geometry can be considered to be a distorted octahedron, XIV, with the main group atom in a cis position with respect to the π -allyl group. If the π -allyl ligand is assumed to be tridentate (and the available structural data suggest that the three carbon atoms are approximately equidistant), then the coordination of the iron atom is seven, with all

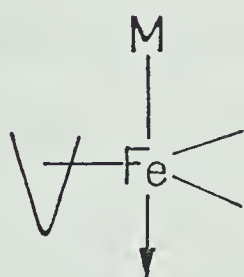


carbonyl groups cis to each other and the central carbon atom of the π -allyl group located above one of the triangular faces of an octahedron, forming a capped octahedron, XV. More simply, the geometry can be assumed to be a distorted trigonal bipyramid, with the main group atom in an axial position and cis to the π -allyl group, if one assumes that the π -allyl group is formally a monodentate ligand, (XVI).

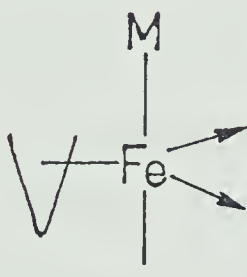
Since the π -allyl group in $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{MR}_3$ has some freedom of rotation about the π -allyl-iron bond as will be discussed later, the idealized geometry XVI was adopted here for purposes of discussion. The choice of the

geometry XVI will simplify the matter and not cause serious problems in the further discussion. The final solution for the question of the exact geometry of $\pi\text{-C}_3\text{H}_5\text{-Fe(CO)}_3\text{MR}_3$ will require a complete structural study by X-ray diffraction.

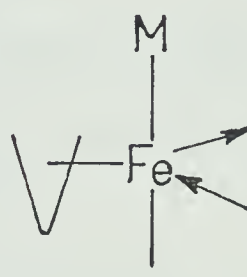
On the basis of the symmetry of $\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_3\text{MR}_3$, three infrared-active bands in the carbonyl stretching region are predicted. These three modes are shown in XVII - XIX.


 \hat{A}_{ax}

XVII


 \hat{A}_{eq}

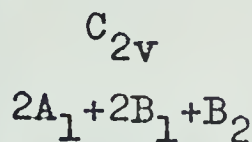
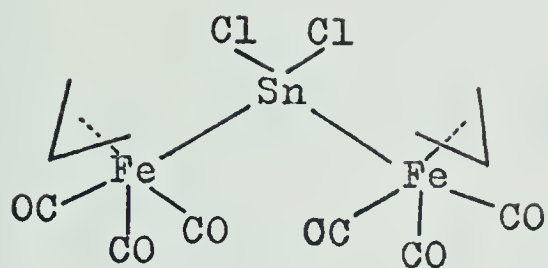
XVIII


 \hat{A}''

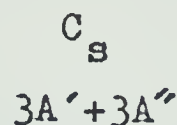
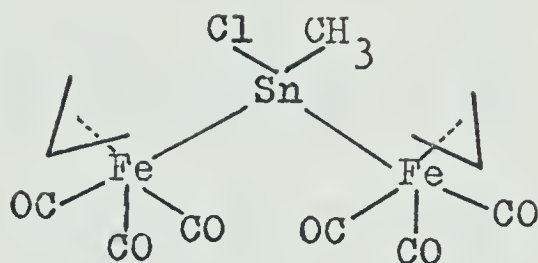
XIX

In the bis(π -allyltricarbonyliron) derivatives, the symmetry is C_{2v} if there is a two-fold rotation axis in the mirror planes, such as $\text{Cl}_2\text{Sn}[\text{Fe(CO)}_3(\pi\text{-C}_3\text{H}_5)]_2$, and C_s otherwise, such as $\text{MeClSn}[\text{Fe(CO)}_3(\pi\text{-C}_3\text{H}_5)]_2$. The number of infrared active bands predicted for the bis(π -allyltricarbonyliron) derivatives on the basis of their symmetries are shown in XX and XXI.

The observed carbonyl stretching frequencies together



XX



XXI

with their relative intensities are listed in Table IV and V, and a selection of typical spectra are shown in Figures 22 - 47 at the end of Chapter V.

It can be seen that many of the spectra are complex showing more bands than would be expected on the basis of their symmetries. Indeed, in most cases there are more carbonyl stretching bands than there are carbon monoxide groups in the molecules. The most striking example is provided by $\text{PhCl}_2\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ in which a total of six terminal stretching bands are observed. Repeated recrystallization and chromatography did not change its spectrum. Moreover, its NMR spectrum exhibited only one set of π -allyl resonances and showed no temperature dependence down to -80° (see Section B of this Chapter).

The appearance of more than three carbonyl stretching bands for a compound possessing only three carbonyl

TABLE IV

Carbonyl Stretching Frequencies for Mono(π -allyltricarbonyliron) Derivatives.^a

Compound	$\nu(\text{CO}), \text{ cm}^{-1}$, with relative intensity ^b		
	A'	A'	A''
$\text{F}_3\text{CFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	2090 (8.6)	2032 (10)	2028 (8.7)
$\text{C}_3\text{F}_7\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	2088 (7.5)	2034 (7.7)	2027 (10)
	2086 (8.4)		
$\text{Cl}_3\text{SiFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	2076 (9.8)	2028 (8.4)	2013 (10)
$\text{Cl}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	2083 (10)	2034 (9.6)	2028 (10)
$\text{Br}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	2081 (9.9)	2032 (7.8)	2027 (10)
$\text{Cl}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	2083 (sh)	2033 (4.2)	2021 (9.6)
	2077 (10)	2029 (8.2)	
$\text{Br}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	2081 (sh)	2033 (3.2)	2020 (9.5)
	2077 (10)	2028 (8.4)	
$\text{Ph}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	2047 (10)	1992 (8.1)	1977 (9.2)
$\text{Me}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	2042 (9.2)	1985 (8.2)	1968 (10)
$\text{Ph}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	2042 (10)	1986 (8.5)	1967 (9.2)
$\text{Me}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	2037 (9.2)	1979 (8.5)	1959 (10)
	2032 (4.7)	1976 (sh)	
$\text{Ph}_3\text{PbFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$	2040 (10)	1985 (7.2)	1972 (7.9)

continued

TABLE IV (continued)

	A'		A'		A''	
PhCl ₂ GeFe(CO) ₃ (π-C ₃ H ₅)	2073	(9.5)	2023	(7.7)	2009	(8.3)
	2069	(10)	2017	(8.6)	2003	(10)
MeCl ₂ GeFe(CO) ₃ (π-C ₃ H ₅)	2074	(5.2)	2026	(4.5)	2009	(4.9)
	2067	(9.6)	2016	(8.6)	1999	(10)
Me ₂ ClGeFe(CO) ₃ (π-C ₃ H ₅)	2061	(sh)	2003	(9.6)	1981	(10)
	2055	(9.9)	1998	(sh)		
Ph ₂ ClGeFe(CO) ₃ (π-C ₃ H ₅)	2062	(sh)	2007	(8.2)	1986	(8.4)
	2058	(10)	2000	(sh)		
PhCl ₂ SnFe(CO) ₃ (π-C ₃ H ₅)	2069	(8.0)	2025	(sh)	2010	(sh)
	2065	(10)	2021	(5.7)	2004	(6.9)
			2015	(8.5)	1998	(9.8)
PhBr ₂ SnFe(CO) ₃ (π-C ₃ H ₅)	2068	(7.1)	2025	(sh)	2010	(sh)
	2064	(10)	2020	(5.0)	2004	(5.7)
			2014	(7.6)	1998	(9.2)
PhI ₂ SnFe(CO) ₃ (π-C ₃ H ₅)	2065	(sh)	2022	(sh)	2008	(sh)
	2062	(10)	2017	(5.0)	2004	(sh)
			2012	(7.6)	1997	(9.3)

a All spectra measured in cyclohexane solution.

b Figures in parentheses are relative heights of bands measured on a linear transmittance scale, taking strongest band as 10. sh = shoulder.

TABLE V

Carbonyl Stretching Frequencies for Bis(π -allyltricarbonyliron) Derivatives ^a

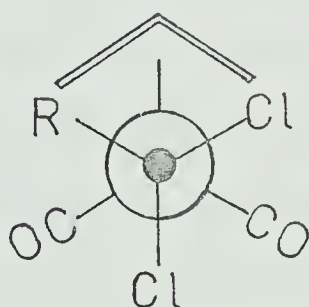
Compound	$\nu(\text{CO})$, cm^{-1} , with relative intensity ^b	
$\text{Br}_2\text{Ge}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2^{\text{C}}$	2075 (10)	2062 (7.6)
	2003 (5.3)	1984 (4.9)
$\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	2068 (9.3)	2054 (sh)
	2016 (sh)	2011 (9.0)
	1992 (5.7)	1982 (4.4)
$\text{I}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	2066 (9.8)	2048 (10)
	2088 (sh)	1998 (5.3)
$\text{MeClSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	2057 (6.3)	2051 (5.8)
	1998 (sh)	1991 (10)
	1964 (4.2)	
$\text{MeBrSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	2057 (6.3)	2051 (5.8)
	1996 (sh)	1990 (10)
	1965 (5.3)	
$\text{PhClSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	2058 (9.1)	2055 (5.4)
	2000 (6.0)	1995 (6.0)
	1966 (4.7)	
$\text{PhBrSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	2058 (9.0)	2054 (5.4)
	1999 (6.1)	1993 (6.2)
	1966 (4.6)	
$\text{Ph}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	2050 (sh)	2046 (8.2)
	1993 (sh)	1985 (9.3)
$\text{Ph}_2\text{Pb}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$	2048 (sh)	2045 (7.0)
	1990 (sh)	1985 (7.7)

continued

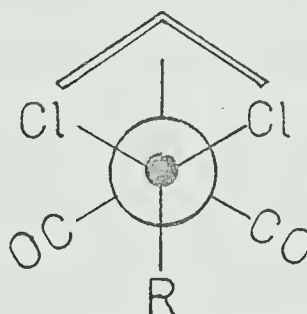
FOOTNOTES TO TABLE V

- a All spectra measured in cyclohexane solution unless otherwise noted.
- b Figures in parentheses are relative heights of bands measured on a linear transmittance scale, taking strongest band as 10.
- c In methylene chloride solution.
-

groups leads one to postulate that isomers are present. This situation appears similar to that observed in other cases where it is generally accepted that the extra bands are due to the presence of conformational isomers. For example, the unsymmetrical substituents on $\text{MeCl}_2\text{SiFe}(\text{CO})_2-(\pi\text{-C}_5\text{H}_5)$ (66), $\text{PhBr}_2\text{SnCo}(\text{CO})\text{Br}(\pi\text{-C}_5\text{H}_5)$ (67), and $\text{THF I}_2\text{InFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (68) have been explained in this way. In the present work, possible conformational isomers of π -allyl compounds are as shown in Newman projection as XXII and XXIII.



XXII



XXIII

This novel conformational effect on the terminal carbonyl stretching frequencies was more evident in $\text{RCl}_2\text{GeFe}(\text{CO})_3-(\pi\text{-C}_3\text{H}_5)$ than in $\text{R}_2\text{ClGeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ (where $\text{R} = \text{Me}, \text{Ph}$) and the separation of the two bands ranged from 4 to 10 cm^{-1} , and they were not resolved in polar solvents such as chloroform, methylene chloride and acetone. It is, however, not clear why the carbonyl group trans to the RCl_2Ge group experiences the same conformational splitting as the carbonyl groups cis to the RCl_2Ge group. A possible explanation

for this is that the unique carbonyl group is not in the exact trans position, being oriented so that the \angle Ge-Fe-C bond angle is no longer 180° . This may be expected from the parameters of the crystal structure of $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$ in which the bond angle of \angle I-Fe-C is 170° (52).

In the corresponding unsymmetrical tin derivatives, the infrared spectra are even more complex, that is, at least two additional shoulder peaks were observed. To account for this unexpected feature, variable temperature NMR studies of these derivatives were examined, and it was found that the NMR spectra were temperature dependent, showing two sets of π -allyl resonances at low temperature. Rapid averaging of two conformations of the π -allyl group accounts for the simple NMR spectra at room temperature. This provided evidence for an additional conformational isomerism (the isomerism of the π -allyl group will be discussed in more detail in Section B of this Chapter). Thus, in the tin derivatives two independent conformational isomerisms are taking place simultaneously; (i) an isomerism by the tin-iron bond rotation, (ii) an isomerism by the rotation about an axis through the π -allyl plane.

A similar conformational effect of a π -allyl group on the terminal carbonyl stretching frequencies has recently been noted by Davison and Rode (69) in the compound $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2(\pi\text{-C}_3\text{H}_5)$, which showed four infrared

carbonyl stretching frequencies. These authors concluded from an NMR study over a range of temperature that the doubling of carbonyl bands is due to the presence of two conformers involving a configurational equilibrium between two differently oriented π -allyl groups.

It is interesting to note that the replacement of the RX_2Sn group by the X_3Sn group eliminates the conformational effect due to the tin-iron bond rotation and reduces the number of carbonyl stretching bands. The observed spectra of $Cl_3SnFe(CO)_3(\pi-C_3H_5)$ and $Br_3SnFe(CO)_3(\pi-C_3H_5)$ nonetheless showed five bands including one shoulder peak, and the extra bands were very probably due to the conformational effect of the π -allyl group; NMR evidence supports this conclusion. Thus, the observation provided evidence that the band splitting due to the conformational effect of the π -allyl group is similar in magnitude to that resulting from tin-iron bond rotation; both are in the range of 5 to 10 cm^{-1} .

On the contrary, $Cl_3SiFe(CO)_3(\pi-C_3H_5)$, $Cl_3GeFe(CO)_3(\pi-C_3H_5)$ and $Br_3GeFe(CO)_3(\pi-C_3H_5)$ showed no evidence for the presence of an extra carbonyl stretching band; only three bands were observed, and this is again entirely consistent with NMR studies of these three compounds which exhibit only one set of allyl resonances at low temperature (vide infra).

The assignment of the observed carbonyl stretching bands to the three predicted modes (A'_{eq} , A'_{ax} , A'') could be done as follows. The highest frequency band may be assigned to A'_{eq} mode. The basis for this assignment is the assumption that the mode in which the greatest number of carbonyl groups are stretching simultaneously will have the highest frequency.

In the assignment of the intermediate and the lowest frequency bands, valuable information could be obtained by studying the degree of depolarization of Raman lines, and this was done in the case of $\text{Ph}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$. It is well known that Raman lines corresponding to totally symmetric vibrations are polarized, while those corresponding to non-totally symmetric vibrations are depolarized (70). More specifically, the degree of depolarization of totally symmetric Raman lines has a value between 0 and 6/7, while for non-totally symmetric Raman lines, it is 6/7. Polarization in the Raman spectrum of $\text{Ph}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ is shown in Figure 4. The spectrum at the top in Figure 4 was obtained with the analyzer transmitting only light polarized parallel to the xy plane (assuming the z axis to coincide with the exciting beam) and the spectrum at the bottom was obtained with the analyzer transmitting only light polarized perpendicular to the xy plane. It is seen that there is a noticeable difference of intensity in the two Raman spectra for the highest and the intermediate fre-

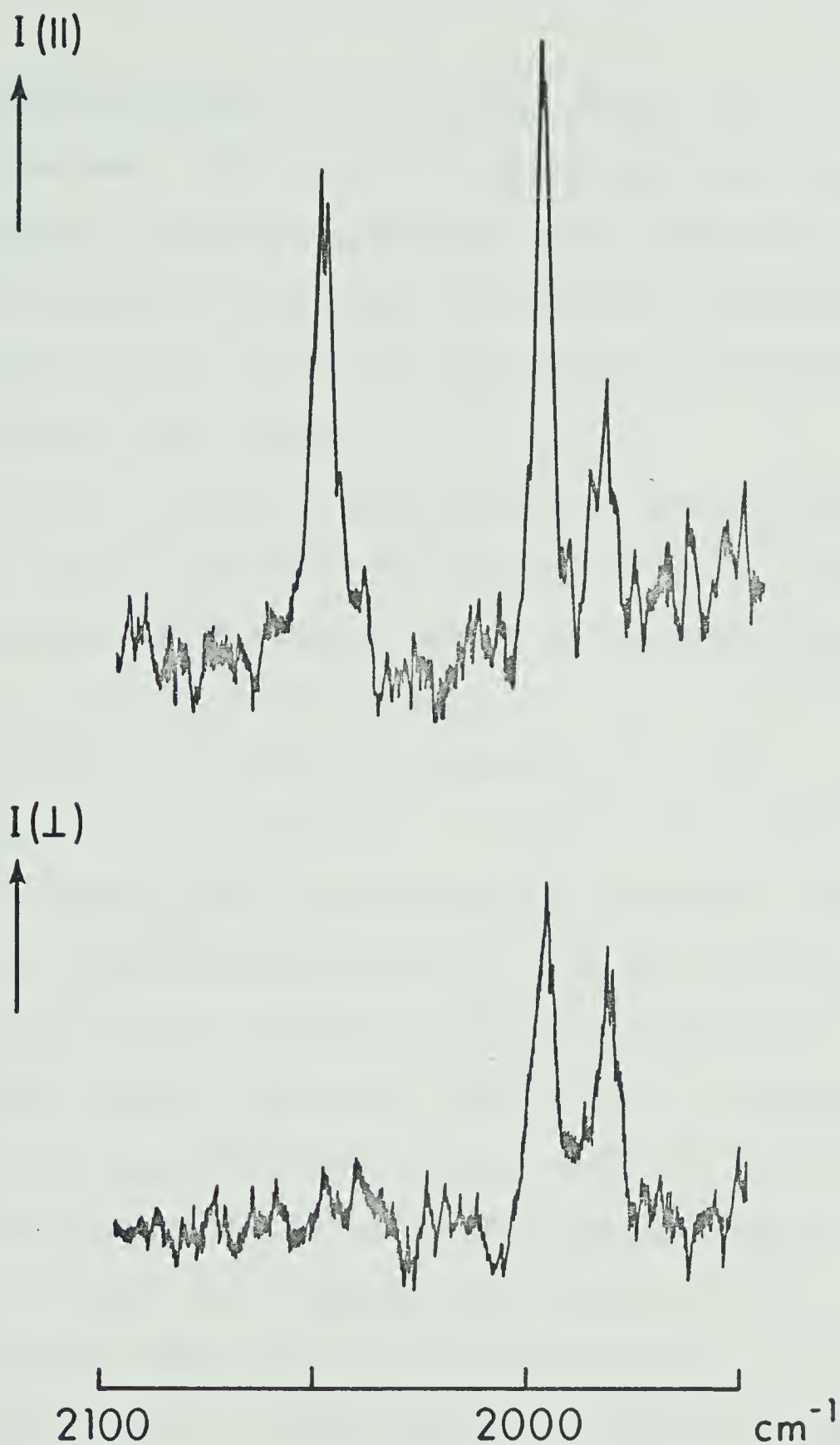


FIGURE 4. Polarization in the Raman spectrum of $(\text{C}_6\text{H}_5)_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ in cyclohexane. CARSON, Ar-Kr Laser Source, Spex 1401 Double Spectrometer.

quency lines, whereas for the lowest Raman line it is approximately the same. The latter is depolarized and corresponds to non-totally symmetric vibration. This observation does establish definitely that the intermediate frequency band corresponds to the A' mode and that the lowest frequency band corresponds to the A'' mode.

Carbonyl stretching frequencies of metal carbonyl derivatives, $LM(CO)_X$, depend upon the nature of L. This has been demonstrated by various series of compounds, such as $(Ph_nCl_{3-n}P)_3Mo(CO)_3$ (71), $XMn(CO)_5$ ($X = Cl, Br, I$ etc.) (72), $R_nX_{3-n}SnMn(CO)_5$ (73) and $R_nX_{3-n}MCo(CO)_4$ ($X = Cl, Br, I$, $R = Me, Ph$, $M = Ge, Sn$) (68). In these series, the carbonyl stretching frequencies show remarkable linearity when plotted against the electronegativities of L or the sum of electronegativities of the halogens attached to germanium or tin.

In the present work, the same effect was observed for the series, $R_nX_{3-n}MFe(CO)_3(\pi-C_3H_5)$, where $M = Ge$ or Sn . A plot of the sum of the Allred-Rochow electronegativities of halogens attached to M against the frequency of A'_{eq} mode gave a linear relationship as shown in Figure 5 and Figure 6. As can be seen in these Figures, a similar dependence was observed between the sum of halogen electronegativities and the mean carbonyl stretching frequencies, ν_m , given by $(1/3)[\nu(A'_{eq}) + \nu(A'_{ax}) + \nu(A'')]$, where the terms in square brackets represent the observed frequencies of the corresponding modes. The influence of the nature of $R_nX_{3-n}M$ on

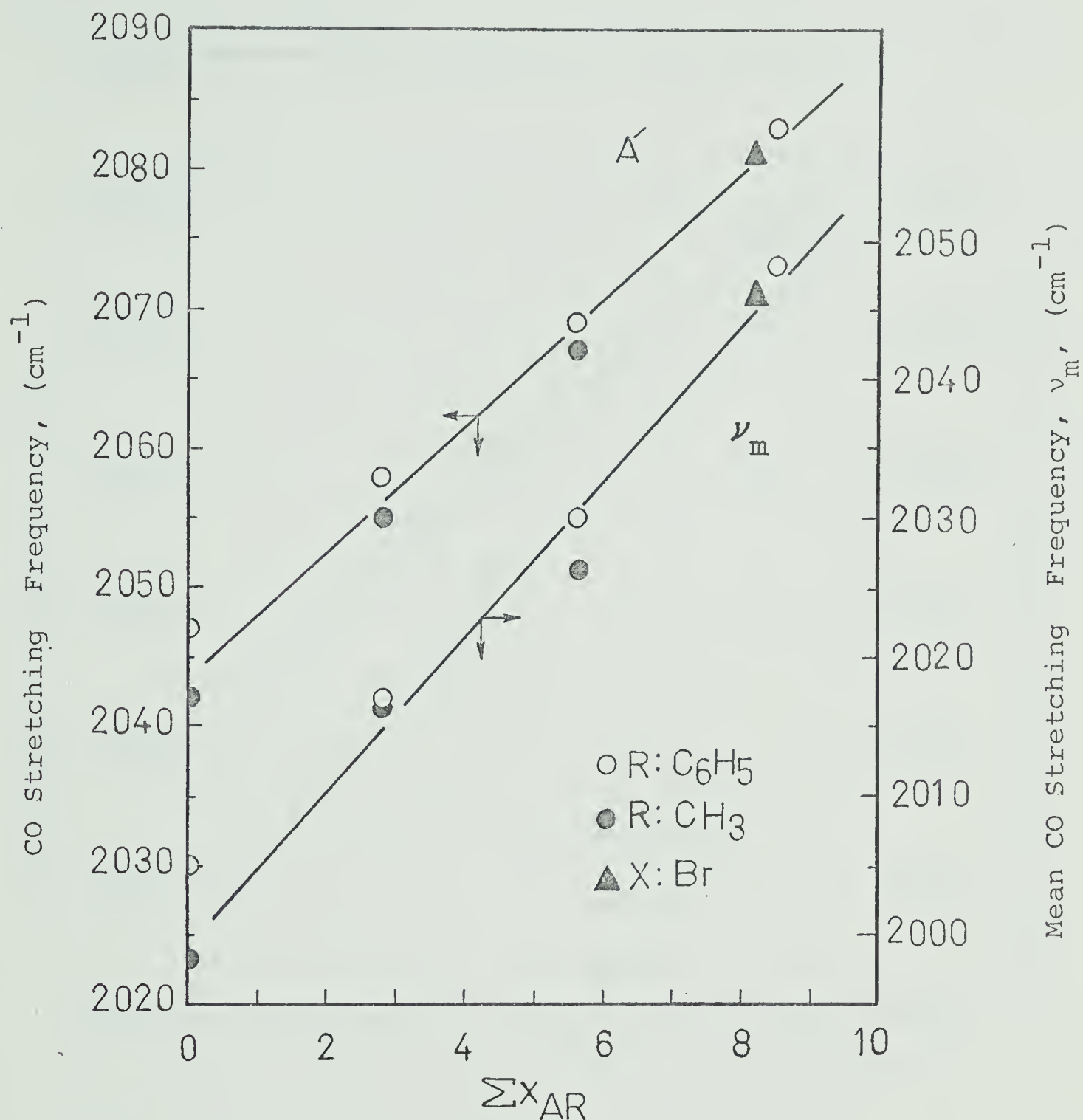


FIGURE 5. The CO stretching frequency of A'_{eq} mode and the mean CO stretching frequency, ν_m , versus the sum of halogen electronegativities for the $R_nX_{3-n}\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$. In case where the spectrum is complex, the value plotted for A'_{eq} is the stronger component of the doublet.

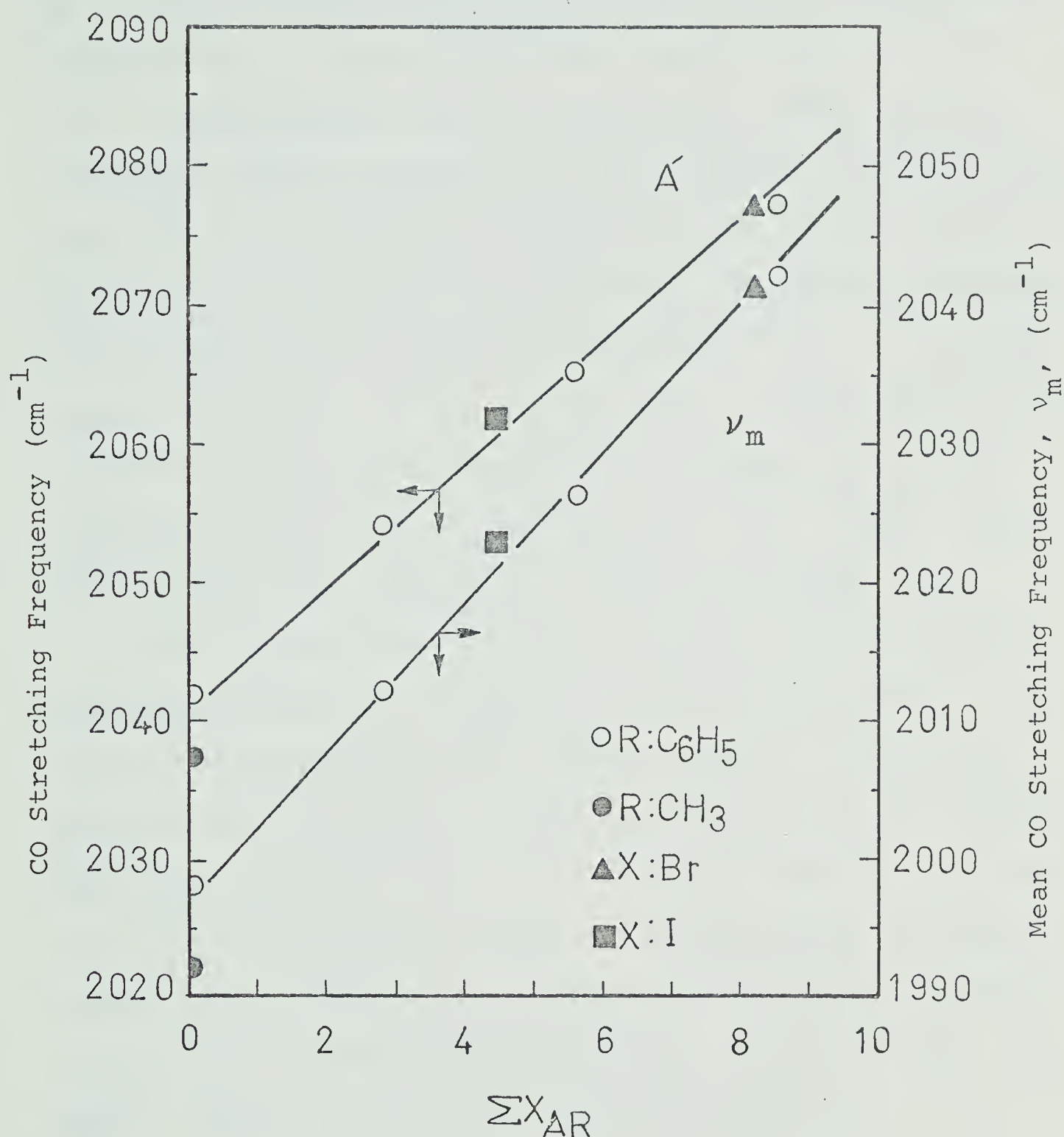


FIGURE 6. The CO stretching frequency of A'_{eq} mode and the mean CO stretching frequency, ν_m , versus the sum of halogen electronegativities for the $R_n X_{3-n} \text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$. In case where the spectrum is complex, the value plotted for A'_{eq} is the stronger component of the doublet.

ν_m was also noted recently by Patmore (68) in the series $R_nX_{3-n}MCo(CO)_4$, where $M = Ge, Sn$; trends very similar to those in the present work were observed. These results indicate a marked dependence of the carbonyl stretching frequency of $R_nX_{3-n}MFe(CO)_3(\pi-C_3H_5)$ upon the nature of $R_nX_{3-n}^M$. The observed variation of the carbonyl stretching frequency can be explained in terms of variations of $d_{\pi} \rightarrow \pi^*$ overlap between Fe and CO. There are two ways in which this can be influenced by $R_nX_{3-n}^M$, one involving changes in the Fe-M π -bonding, and the other involving the Fe-M σ -bond. These effects have been described in detail by Graham (74).

The infrared spectra of bis(π -allyltricarboxyliron) derivatives showed very complex intensity patterns in the carbonyl stretching region, and no attempt to assign the observed bands was made, except to suggest that the highest frequency band may be due to the totally symmetric stretching of all six carbonyl groups. The complexity presumably arises from a combination of the stereochemical nonrigidity of the π -allyl groups with rotational isomerism about the bonds between iron and the group IV elements.

B. Nuclear Magnetic Resonance Spectra

INTRODUCTION

The NMR spectra of allyl metal complexes have been considered diagnostic for modes of bonding between the allyl ligand and the metal atom. Several types of NMR spectra of allyl ligands bonded to metal atoms are known, and these are of following types: (i) $ABCX_2$ spectra; σ -allyl transition metal compounds such as $\sigma-C_3H_5Mn(CO)_5$ (75), and $\pi-C_5H_5Fe(CO)_2^-(\sigma-C_3H_5)$ (7). (ii) A_4X spectra; allylmagnesium bromide (Grignard reagent) (76), allyllithium (77) and $Zr(\pi-C_3H_5)_4$ (78). These compounds undergo "dynamic" behavior involving a rapid interconversion at room temperature or higher. (iii) A_2M_2X spectra; $\pi-C_3H_5Mn(CO)_4$ (75), $\pi-C_3H_5Co(CO)_3$ (20) and $(\pi-C_3H_5PdCl)_2$ (79). The proton spectra of this group consists of two doublets (intensity 2:2) and complex multiplet (intensity 1).

The proton spectra of the π -allyl transition metal complexes of interest in this work are of type (iii). Fortunately, chemical shift differences among non-equivalent protons are much larger than the spin-spin coupling constants, and therefore a first-order analysis of the spectra is possible. The π -allyl portion of the proton spectrum of $PhCl_2GeFe(CO)_3(\pi-C_3H_5)$ is shown as a typical example in Figure 7. The two doublets represent the $H_2(H_2')$ and $H_3(H_3')$ and the complex multiplet represents the H_1 .

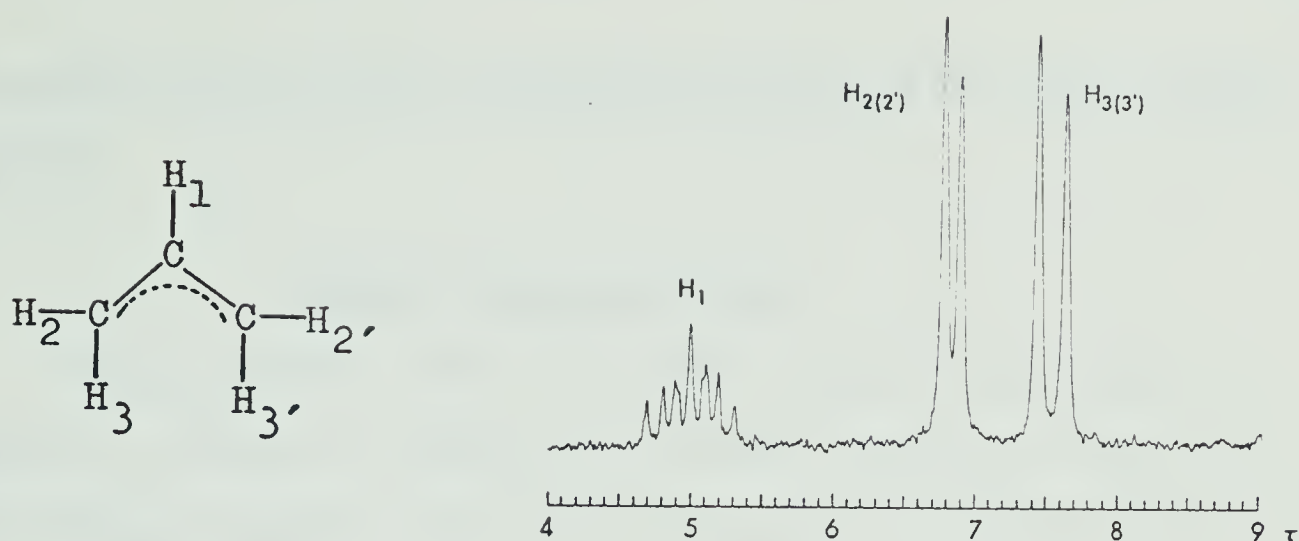


Figure 7. A typical NMR spectrum of a π -allyl metal group with the customary numbering of the protons.

The assignment of spectral lines to H_2 ($H_{2'}$) and H_3 ($H_{3'}$) is based on the relative strength of cis- and trans-coupling constants in substituted ethylenic systems (80). The coupling constants, J_{12} ($J_{12'}$) and J_{13} ($J_{13'}$) are usually on the order of ~ 7 and ~ 11 cps. respectively (1). The coupling constants J_{23} and $J_{23'}$ are vanishingly small and it is this fact which simplifies the spectrum from the much more complex $AA'MM'X$ type.

Anomalous spectra for a π -allyl ligand, however, are occasionally found, and these phenomena have been explained by the stereochemical nonrigidity of the π -allyl moiety (56,69,81). Evidence for this is primarily presented by the temperature dependence of the NMR spectra and their eventual collapse with rising temperature to either dynamic A_4X or A_2M_2X spectra. In some of the compounds obtained in the present work, the π -allyl moiety has been found to be stereochemically non-rigid, and this has already been invoked

to explain some of the unexpected features of the infrared spectra.

RESULTS AND DISCUSSION

In the present work, the NMR spectra were employed mainly in order to account for several unusual features in the infrared spectra and also as an aid in the characterization of compounds. The NMR spectra are, therefore, discussed here with reference to the infrared spectra.

After the commencement of the present work, detailed NMR studies of a series of π -allyltricarboxyliron halides and related compounds were reported (56,81) as well as the crystal structure of the iodide (52), and the halides were shown to exist in the form of two rotational isomers. Since the results of the preliminary investigation of the NMR spectra of these compounds in the present work are almost identical to those reported, they are not presented in this Thesis.

For some years, it has been known that the infrared spectrum of the iodide exhibited four carbonyl stretching bands, and the suggestion was made that a dimeric species was involved (34). In the course of the present work, the presence of a fourth carbonyl band in the iodide was confirmed, and it was attributed to a conformational effect involving the allyl group. The observed NMR spectra support this interpretation, although the Russian workers did not comment on this aspect of the problem (56,81).

All of the NMR spectra obtained in the present work exhibited A_2M_2X pattern at room temperature. The observed chemical shifts and spin-spin coupling constants of a selection of the spectra obtained are listed in Table VI. The NMR spectra of many of the tin derivatives showed temperature dependence and gave two sets of π -allyl resonances at low temperature. The chemical shift values given in Table VI for the tin derivatives are values obtained from the spectra at room temperature, and thus represent average values of two isomers.

The chemical shift values of the intense doublet at the higher field ranged from τ 7.39 to τ 8.06 and a spin-spin coupling constant in the range 11.4 - 12.0 cps. was observed. The other intense doublet appeared in the region of τ 6.45 to τ 7.41 and had a spin-spin coupling constant of 6.5 - 7.0 cps. The former doublet was assigned to the $H_3(H_{3,})$ (anti-proton) and the latter, therefore, to the $H_2(H_{2,})$ (syn-proton). The multiplet around τ 5.0 due to H_1 was usually not well resolved.

This assignment was made for the same reasons stated by Nesmeyanov et al. in their study of π -allyltricarboxyl-iron halides (81). The anti-protons appear at higher field since they are nearer to the metal and halogen atoms; the magnetic anisotropy of the latter atoms should substantially contribute to the shielding of the anti-protons (81). Furthermore, the observed spin-spin coupling constants

TABLE VI

Chemical Shifts and Coupling Constants ^a						
Compound	H ₁	H ₂	H ₃	CH ₃	J ₁₂	J ₁₃
Cl ₃ SnFe(CO) ₃ (π-C ₃ H ₅)	4.75	6.45	7.42	-	7.0	12.0
PhCl ₂ SnFe(CO) ₃ (π-C ₃ H ₅)	4.59	6.74	7.39	-	7.0	12.0
Br ₃ SnFe(CO) ₃ (π-C ₃ H ₅)	4.78	6.52	7.39	-	6.0	12.0
PhBr ₂ SnFe(CO) ₃ (π-C ₃ H ₅)	4.85	6.72	7.52	-	7.0	12.0
PhI ₂ SnFe(CO) ₃ (π-C ₃ H ₅)	4.97	6.86	7.51	-	7.0	12.0
Ph ₃ SnFe(CO) ₃ (π-C ₃ H ₅)	4.99	7.36	7.96	-	7.0	11.5
Me ₃ SnFe(CO) ₃ (π-C ₃ H ₅)	5.33	7.41	8.06	9.65	6.5	11.4
Cl ₃ GeFe(CO) ₃ (π-C ₃ H ₅)	4.82	6.55	7.42	-	7.0	12.0
PhCl ₂ GeFe(CO) ₃ (π-C ₃ H ₅)	4.94	6.80	7.56	-	6.5	12.0
MeCl ₂ GeFe(CO) ₃ (π-C ₃ H ₅)	4.94	6.87	7.57	8.67	7.0	12.0
Ph ₂ ClGeFe(CO) ₃ (π-C ₃ H ₅)	5.19	7.13	7.75	-	7.0	12.0
Me ₂ ClGeFe(CO) ₃ (π-C ₃ H ₅)	5.21	7.07	7.78	9.12	7.0	11.8
Me ₃ GeFe(CO) ₃ (π-C ₃ H ₅)	5.22	7.40	8.05	9.60	6.5	11.5
Ph ₃ GeFe(CO) ₃ (π-C ₃ H ₅)	5.10	7.43	7.93	-	6.0	12.0

continued

TABLE VI (continued)

Compound	H ₁	H ₂	H ₃	CH ₃	J ₁₂	J ₁₃
Cl ₂ Sn[Fe(CO) ₃ (π-C ₃ H ₅)] ₂	4.75	6.60	7.59	-	7.0	12.0
MeClSn[Fe(CO) ₃ (π-C ₃ H ₅)] ₂	5.02	6.88	7.81	8.92	7.0	11.5
I ₂ Sn[Fe(CO) ₃ (π-C ₃ H ₅)] ₂	4.94	6.68	7.55	-	7.0	12.0
Ph ₂ Sn[Fe(CO) ₃ (π-C ₃ H ₅)] ₂	5.18	7.36	8.06	-	6.8	11.8

^a All spectra were taken in CDCl₃ at ambient temperature. Chemical shifts are in ppm relative to tetramethylsilane as 10. The numbering of the protons refers to Figure 7.

$J_{12}(J_{12}')$ and $J_{13}(J_{13}')$ correspond to typical values of cis- and trans-coupling constants in ethylenic systems (80), a fact employed by Moore et al. (82) in the assignment of spectral lines of π -(1-methylallyl)tricarbonylcobalt.

The absence of observable coupling between geminal protons, $H_2(H_2')$ and $H_3(H_3')$, may be explained in terms of the valence-bond treatment of Gutowsky, Karplus and Grant (83) in which the geminal coupling constant is given as a function of the interproton bond angle. This, together with observed values of $J_{12}(J_{12}')$ and $J_{13}(J_{13}')$, would suggest that the five π -allylic protons are in a plane and therefore hybridization of carbon atoms is close to sp^2 .

As noted previously, variable temperature NMR studies of the compounds having more than three terminal carbonyl stretching bands in the infrared spectra were examined in order to account for this unusual infrared behavior. The temperature dependence of the NMR spectra of $\text{PhCl}_2\text{SnFe(CO)}_2-(\pi\text{-C}_3\text{H}_5)$ and $\text{Br}_3\text{SnFe(CO)}_3(\pi\text{-C}_3\text{H}_5)$ are shown in Figures 8 and 9. It can be seen from these Figures that the spectra show two overlapping A_2M_2X patterns at low temperature. This temperature behavior of the NMR spectra of these compounds is essentially the same as that observed for $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_2-(\pi\text{-C}_3\text{H}_5)$ (69); thus structures XXIV and XXV were postulated for two conformations of the molecule. As the temperature was raised the corresponding resonance lines of the two configurations of π -allyl moiety broadened and coalesced to higher temperature spectra which were approximately the

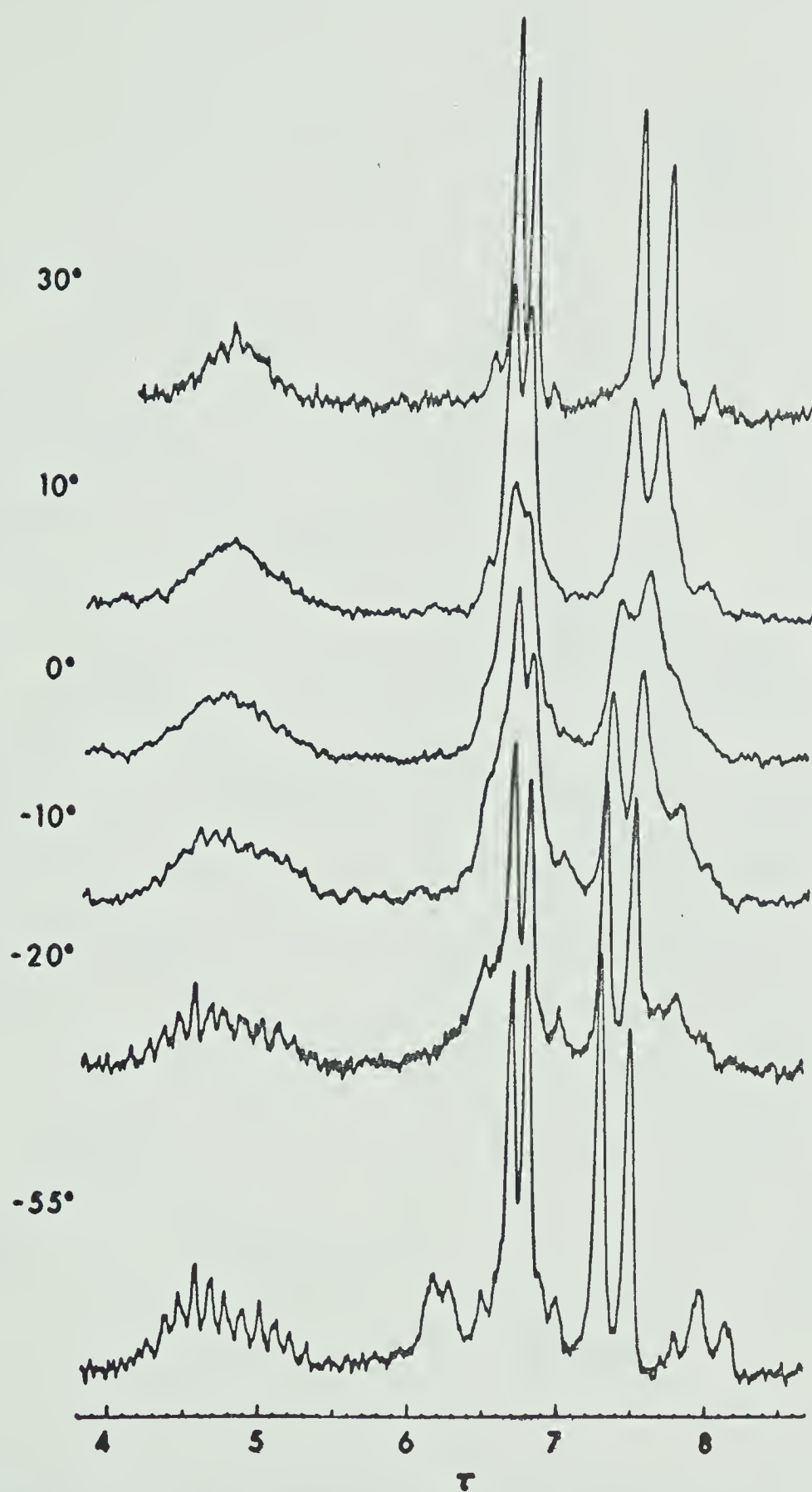


FIGURE 8. The temperature dependence of the NMR spectrum of $\text{PhCl}_2\text{SnFe(CO)}_3(\pi\text{-C}_3\text{H}_5)$ in CDCl_3 .

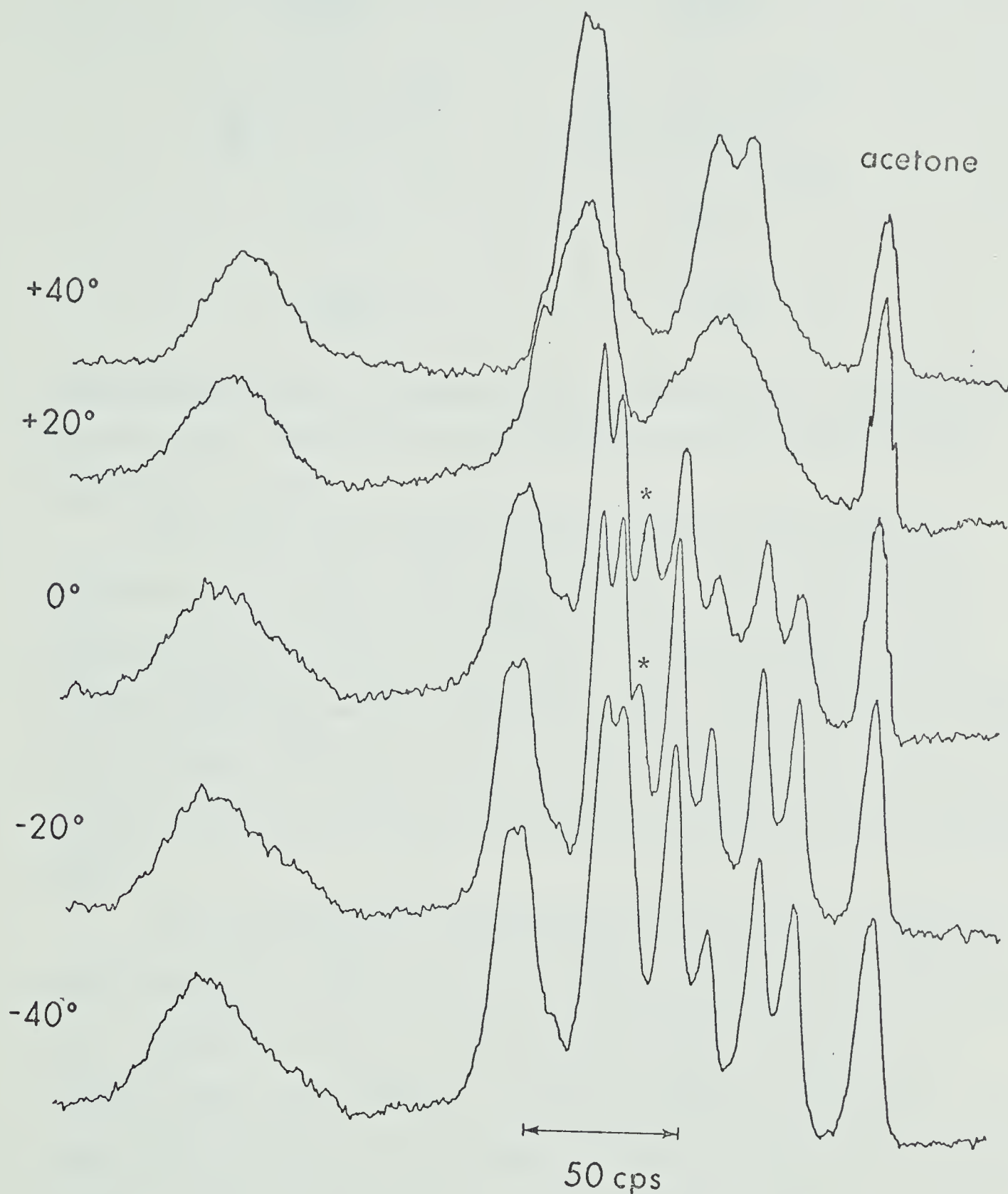
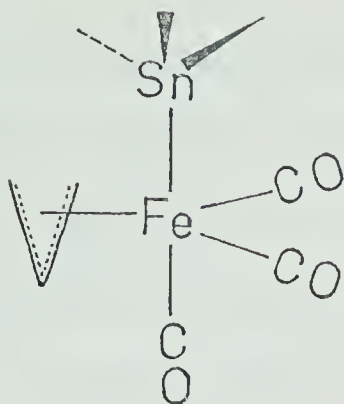
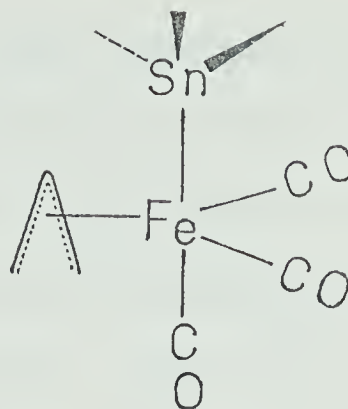


FIGURE 9.

The temperature dependence of the NMR spectrum of $\text{Br}_3\text{SnFe(CO)}_3(\pi\text{-C}_3\text{H}_5)$ in deuterioacetone. The origin of the band which appears at intermediate temperatures (marked with an asterisk) is not understood.



XXIV



XXV

weighted averages of those at low temperature. Equilibrium between the isomers is thus shifted little over the 80° temperature range.

Over the temperature range observed there was no averaging of the syn and anti-protons. This eliminates possible mechanisms for conformer interconversion which require syn-anti proton exchange (78). One possible mechanism involves rotation about an axis through the π -allyl plane; another would involve an intermediate having an 180° dihedral angle.

No concentration dependence of the rate of exchange was detected in CDCl_3 solutions whose concentrations varied by a factor of two at temperatures down to about -50°, showing that the exchange is first order as expected. It was not possible to calculate reliable rotational barriers for the tin derivatives, owing to widely different concentrations of the conformers, and to the relatively poor NMR line shape. However, a rough estimate based on the spectra of Figure 8 gave a value of 9 kcal/mole.

The above observations have already been invoked to explain the infrared spectral behavior. Since it is clear

that the averaging process at room temperature involves an equilibrium between two conformations of the π -allyl moiety, it is not surprising that these conformations are reflected in the terminal carbonyl stretching frequencies and a maximum of six bands would be observed. This was actually seen in $\text{Cl}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ and $\text{Br}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, which exhibited five terminal carbonyl stretching bands including one shoulder and one broad peak.

It is interesting to note that there is no evidence for the temperature dependence of the NMR spectrum of $\text{Ph}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ over the temperature range from 25° to -80° , consistent with the observation of only three terminal carbonyl stretching bands in the infrared spectrum. This is somewhat surprising considering that $\text{PhX}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ and $\text{X}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ ($\text{X} = \text{Cl}, \text{Br}$) gave resonances corresponding to two distinct π -allyl groups at low temperature (ca. -50°). A possible reason for this is that three bulky phenyl groups attached to tin leave only a single sterically reasonable orientation for the π -allyl group. Examination of molecular models based on the available X-ray structural data (52,84) indicated that the interactions between the hydrogen atom on the central carbon of the allyl group in the conformer XXV and ortho-hydrogens of phenyl groups were likely to be much greater than those between the anti-hydrogen atoms and those in the conformer XXIV. This situation is represented in Figure 10.

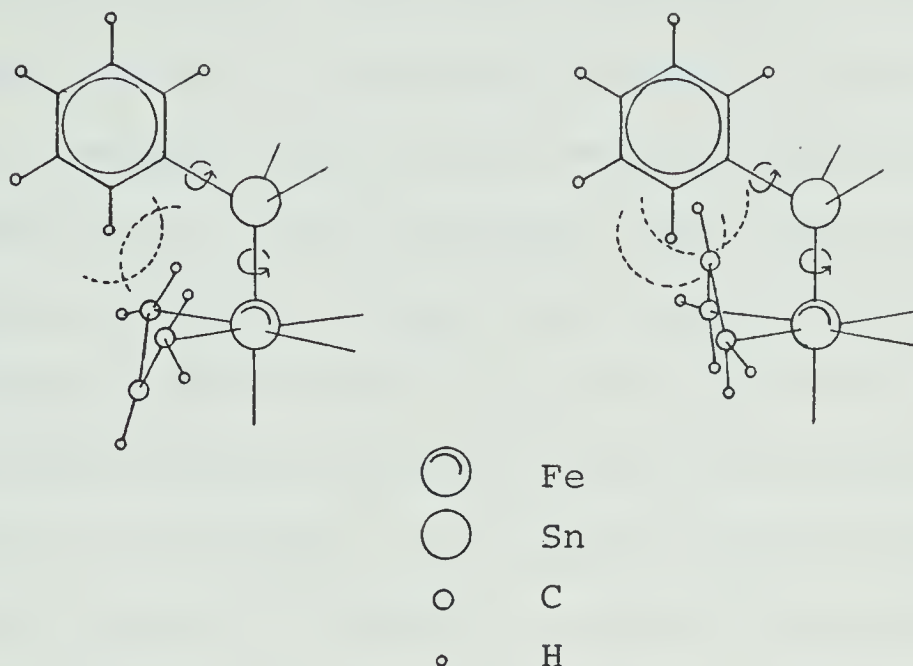


Figure 10. Nonbonded interactions between ortho-hydrogens of phenyl groups and hydrogens of π -allyl group of $\text{Ph}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$: Distances between bonded atoms are drawn approximately proportional to actual values, and dotted semicircles represent Van der Waals radius of hydrogen. Carbonyl and two phenyl groups are not shown.

This could explain the observation that one conformation predominated over the other in $\text{PhCl}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ (see Figure 8).

All the germanium derivatives, $\text{Cl}_3\text{SiFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, and $\text{CF}_3\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ showed no temperature dependent NMR spectra. This indicates that there is only one conformation

of the π -allyl moiety in these molecules. This may perhaps be due to the shorter Fe-M bond distances ($M = \text{Ge}, \text{Si}, \text{C}$), which would result in a greater nonbonded interaction between the hydrogen atom on the central carbon and the substituents on M in the conformer XXV, thus destabilizing XXV relative to XXIV. It may also be possible that the higher electronegativities of M relative to tin decrease the electron density on the iron atom, thus making the π -allyl-iron bond stronger in a formal donor-acceptor sense (the π -allyl group as a donor). Hence, the bonding interaction between them will become greater in the conformer XXIV, considering that the central carbon-iron distance in XXIV will be shorter than in XXV. The latter possibility was employed to explain a regular increase of the minor isomer analogous to XXV in the series $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) as the electronegativities of X decrease (81). The NMR spectrum of $\text{Cl}_3\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ in which the steric factor may be similar to the corresponding tin derivative (the iron-germanium and the iron-tin bond distances are 2.36 and 2.49 Å respectively in $\text{Cl}_2\text{M}[\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)]_2$, where $M = \text{Ge}$ (85), Sn (86)), showed no evidence for conformational isomerism. This suggests that not only steric but also electronic factors are involved. The electronic factor in the present case would account for the electron attracting ability of M (or X_3M), so that a good σ - and π -acceptor such as the Cl_3Ge group would

facilitate the π -allyl-iron bonding interaction. This again leads one to a suggestion similar to that proposed for π -allyltricarboxyliron halides (81). As the following discussion is also consistent with the above explanation, both steric and electronic factors appear to govern the magnitude of the energy difference between the two configurations.

As mentioned previously (in Section A of this Chapter), carbonyl stretching frequencies of $R_nX_{3-n}MFe(CO)_3(\pi-C_3H_5)$ (where $R = Me, Ph, X = Cl, Br, M = Ge, Sn; n = 0-3$) showed a marked dependence on the nature of $R_nX_{3-n}M$ group. Electronegative substituents on M tend to remove electron density from the iron atom and this is reflected in the carbonyl stretching frequencies and also in the chemical shift values of the π -allyl protons. This latter point will now be discussed. The chemical shift values of H_1 , H_2 , and H_3 for $R_nCl_{3-n}GeFe(CO)_3(\pi-C_3H_5)$ ($R = Me, Ph; n = 0-3$) were plotted against the sum of halogen electronegativity ($\sum X_{AR}$) in Figure 11. The H_2 and H_3 chemical shifts correlate well with the electronegativity, while H_1 chemical shifts are much less sensitive to $\sum X_{AR}$.

The carbonyl stretching frequencies in a particular series of compounds are often taken to be a rough measure of the electron density on the metal atom. The latter may also be reflected in the chemical shift values of a group attached to the metal in some way. The carbonyl stretch-

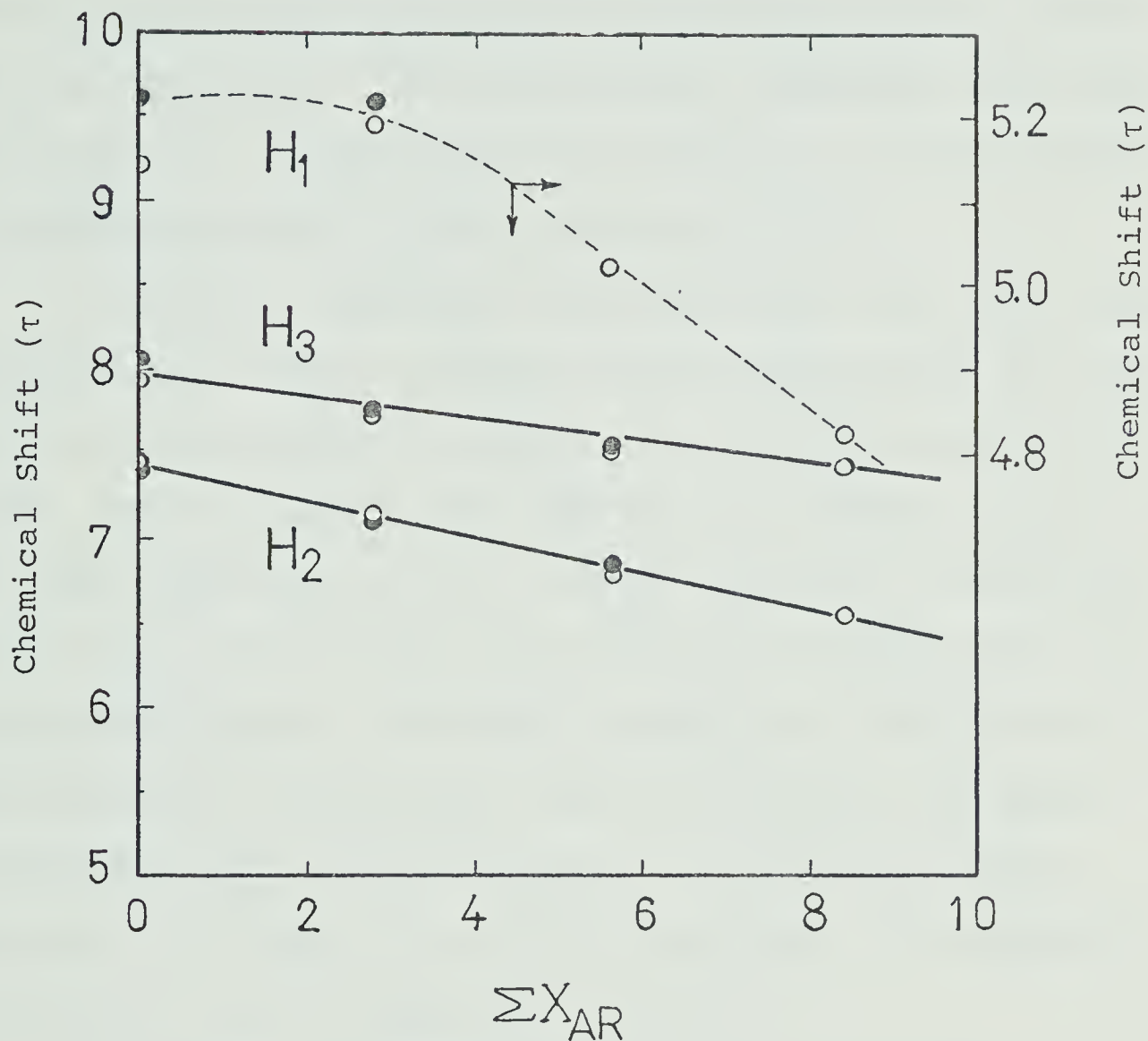


FIGURE 11. The allyl group proton shifts of $R_nCl_{3-n}GeFe(CO)_3(\pi-C_3H_5)$ versus the sum of chlorine electronegativity on the Allred-Rochow scale, $\sum X_{AR}^*$.

(●), R = Me, (○), R = Ph.

*Allred-Rochow values from J. Inorg. Nucl. Chem., 5, 264 (1958).

frequencies (ν) were plotted against the chemical shift values of H_2 and H_3 for the series $R_nCl_{3-n}GeFe(CO)_3(\pi-C_3H_5)$ in Figure 12. There are excellent correlations between carbonyl stretching frequencies and chemical shift values of H_2 as well as H_3 . This observation parallels the chemical shifts of π -cyclopentadienyl protons of a large number of π -cyclopentadienyl metal derivatives (87).

A similar dependence (not presented here) was observed between the sum of halogen electronegativities and the chemical shift values of H_2 and H_3 in the tin derivatives. Use of the "averaged" room temperature resonance values for these compounds led to a rather poor plot. Acetone- d_6 was the only solvent from which the tin compounds did not precipitate before a low enough temperature was achieved. Unfortunately, the multiplet due to an acetone- d_5 impurity made the anti-proton resonance of the minor isomer ambiguous. In $CDCl_3$, CS_2 , $CFCl_3$, or CD_3CN , the compounds precipitated out at about $-20^\circ \sim -30^\circ$.

The temperature dependence of the NMR spectrum of $Ph_2Sn[Fe(CO)_3(\pi-C_3H_5)]_2$ is presented in Figure 13. The temperature behavior is essentially the same as that of mono- $(\pi$ -allyltricarbonyliron) derivatives. The complexity of the infrared spectra of bis derivatives could well be interpreted in terms of the presence of conformers as well.

Finally, a brief comment is presented on the NMR studies of $MeCl_2GeFe(CO)_3(\pi-C_3H_5)$. The latter exhibited

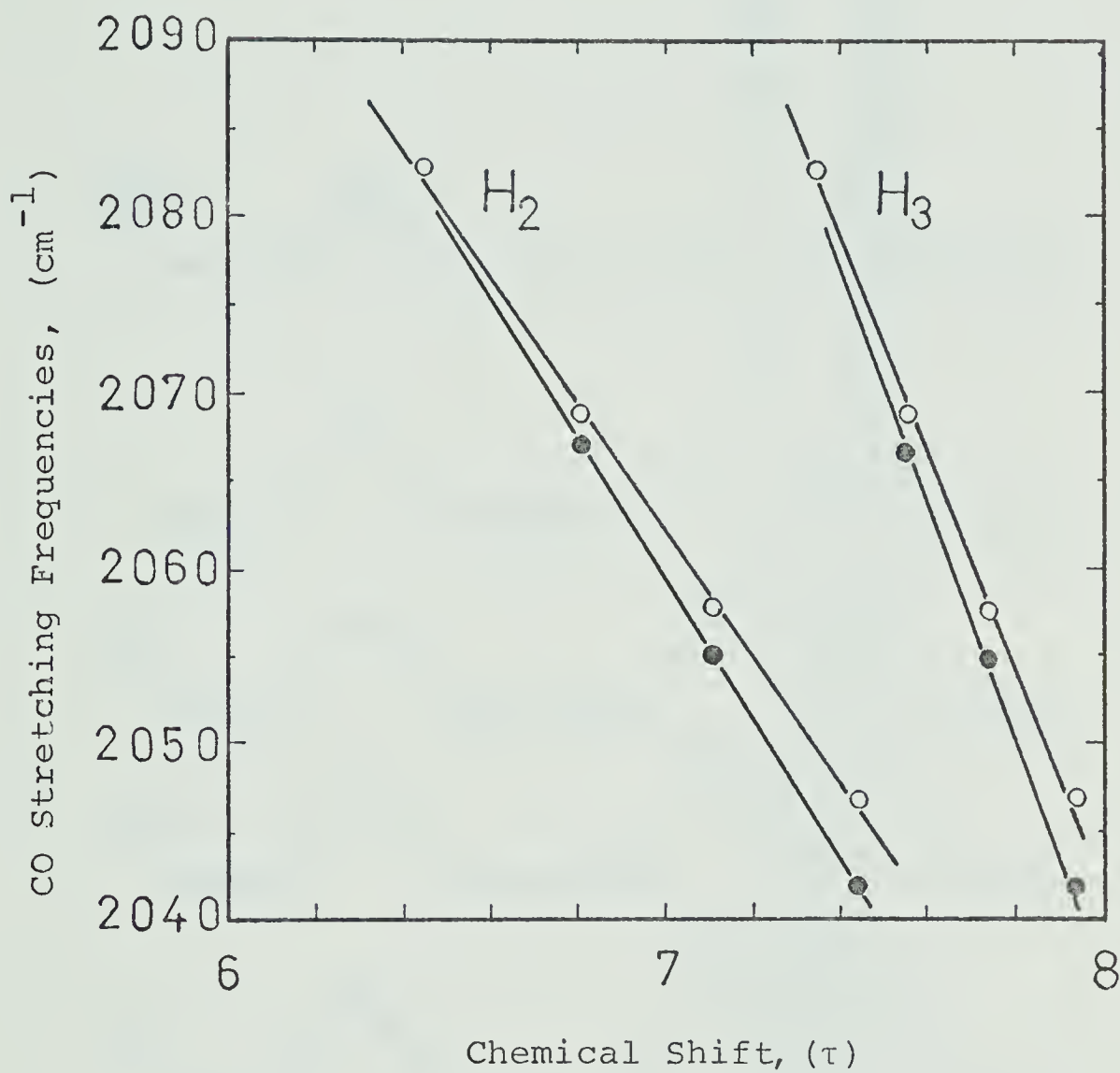


FIGURE 12 The carbonyl stretching frequencies (ν_{eq}) versus the allyl group chemical shifts for the $R_nCl_{3-n}GeFe(CO)_3(\pi-C_3H_5)$ series.
 (●), $R = Me$, (O), $R = Ph$.

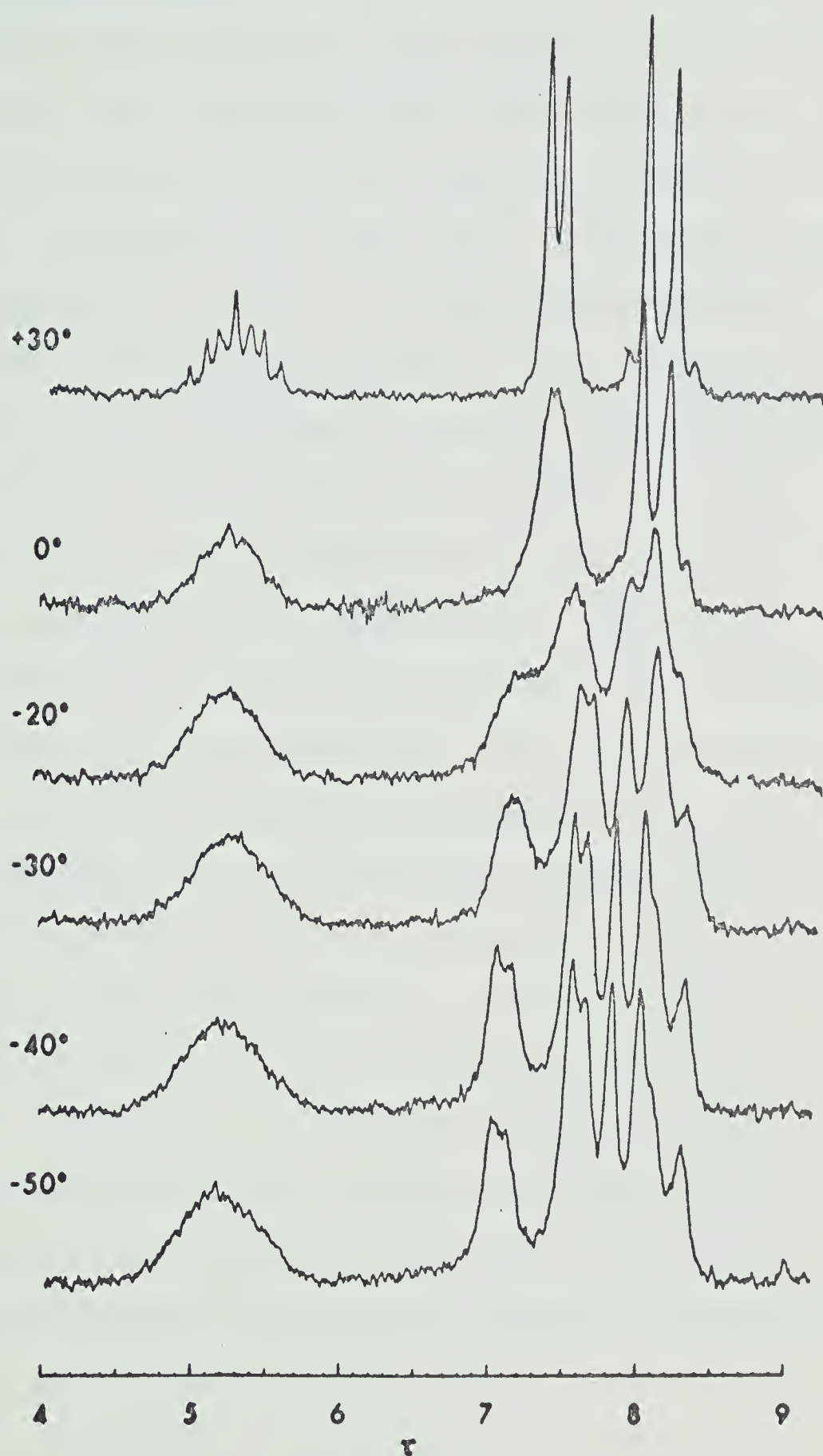


FIGURE 13 The temperature dependence of the NMR spectrum of $\text{Ph}_2\text{Sn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$ in CDCl_3 .

six terminal carbonyl stretching bands, and this was explained by the presence of two isomers involving rotation about the iron-germanium bond. The NMR spectrum, however, exhibited only one methyl resonance as well as one set of π -allyl resonances over the entire temperature range investigated (25° - -80°) in trichlorofluoromethane. Rotation about the iron-germanium bond in this temperature range is evidently not slow enough to permit the observation of the two distinct conformations on the NMR time scale (10^{-4} - 10^{-1} second). It is also possible that only one Ge-Fe conformation is present at low temperature. This is the case with $\text{MeCl}_2\text{GeFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ which exhibits four carbonyl stretching bands at room temperature and only two bands at -40° (88). The likely explanation proposed (89) for this is that the population of the higher energy state is depleted by the Boltzmann principle, before the rate of interconversion of two conformations is slowed enough to permit the observation of the two distinct forms on the NMR time scale. However, in the present work, an attempt to obtain an infrared spectrum at sufficiently low temperature was not successful; six bands were still observed at -20° , at which temperature the compound started precipitating out of the n-pentane solution.

C. Mass SpectraINTRODUCTION

The importance of the mass spectroscopic studies of organotransition metal compounds, apart from the derivation of thermodynamic quantities (90,91,92), lies in establishing molecular formulae and providing information on molecular structure. With the advent of commercially available high resolution mass spectrometers capable of handling compounds with high molecular weights, numerous mass spectra of organometallic carbonyl derivatives have been investigated within the last several years (93).

Mononuclear and purely metal-metal bonded carbonyls show prominent parent ions decomposing by successive loss of carbon monoxide. Compounds with bridging carbonyl groups and weak metal-metal interaction show extensive cleavage to mononuclear ions (94).

In transition metal-main group IV metal compounds, the major fragmentation pathway in most carbonyl derivatives involves loss of all the carbonyl groups before other bonds are broken, although in $\text{Me}_3\text{SnMo}(\text{CO})_3(\pi\text{-C}_5\text{H}_5)$, the molecular ion first loses a methyl group before losing its first carbonyl group (95). Carbonyl halides also exhibit competitive loss of carbonyl and halide from the parent ion, whereas in halogen or sulfur bridged binuclear compounds, the M_2X_2 unit persists unfragmented until loss of

carbonyl groups is complete (96,97).

In carbonyl hydrides, hydrogen may be retained by parent and fragment ions showing fragments due to consecutive loss of carbonyl as well as hydrogen.

In polynuclear carbonyl hydrides, such as $\text{H}_3\text{Mn}_3(\text{CO})_{12}$, $\text{H}_3\text{Re}_3(\text{CO})_{12}$, a carbonyl group is lost more readily than hydrogen. Moreover in the hydrogen bridged complex like $\text{H}_7\text{B}_2\text{Mn}_3(\text{CO})_{10}$, all the bridging hydrogen atoms are retained until four carbonyl groups have been lost (98).

The structures of several unusual compounds derive support from their mass spectra; for example, the mixed metal cluster, $\text{HMCo}_3(\text{CO})_{12}$, ($\text{M} = \text{Fe}, \text{Ru}$) shows that hydrogen-free ions are weak until after fragmentation of the MCo_3 unit. This, together with a metal-hydrogen frequency around 1100 cm^{-1} is in accord with hydrogen being inside the MCo_3 cage (99). Robinson et al. (100) also used mass spectroscopy to characterize the novel compound, $\text{Co}_5(\text{CO})_{15}\text{C}_3\text{H}$.

Mass spectrometry thus provides useful information on the structures of these compounds and is quite often utilized as a means of characterization.

RESULTS AND DISCUSSION

In the present work, mass spectra were employed mainly as an aid in the characterization of compounds. This involved the identification of the observed ions from their mass numbers and a knowledge of the elements present. Interpretation of the mass spectra was greatly facilitated

by the use of a computer program to calculate theoretical peak masses and isotope combination patterns. Some of the isotope combination patterns employed in this work are shown in Figure 14 and 15.

The mass spectra of $\text{Me}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, $\text{PhI}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, $\text{Br}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, $\text{Me}_2\text{ClGeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ and $\text{MeClSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$ were reported in detail in Table VII - XI as representatives of the compounds obtained in the present work. The following general features were observed: (i) Fragments corresponding to consecutive loss of carbonyl groups from the parent ion. (ii) Fragments which had lost an allyl group before losing substituents on tin or germanium were observed in appreciable abundance. (iii) Bis(π -allyltricarbonyliron) derivatives lost one allyl group before loss of carbonyl groups was complete. (iv) $\text{Me}_n\text{Cl}_{3-n}\text{MFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ ($n = 3, 2, 1, 0$, $M = \text{Ge, Sn}$; $n = 3, 2, 1, 0$, $M = \text{Ge}$) showed comparable loss of a methyl, a chlorine, and a carbonyl group from the molecular ions, whereas $\text{Ph}_n\text{X}_{3-n}\text{MFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ ($n = 3, 2, 1, 0$, $M = \text{Ge, Sn}$, $X = \text{Cl}$; $n = 3, 2, 1, 0$, $M = \text{Ge}$, $X = \text{Cl}$) did not show the corresponding fragments due to loss of phenyl groups from the molecular ion.

The mass spectrum of $\text{Me}_3\text{MFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ ($M = \text{Ge, Sn}$) possessed fragments corresponding to $[\text{Me}_3\text{MFe}(\text{CO})_x(\pi\text{-C}_3\text{H}_5)]^+$ ($x = 3, 2, 1, 0$), as well as fragments due to loss of one methyl group. However, fragments which had lost more than one methyl group before all carbonyl groups were lost were

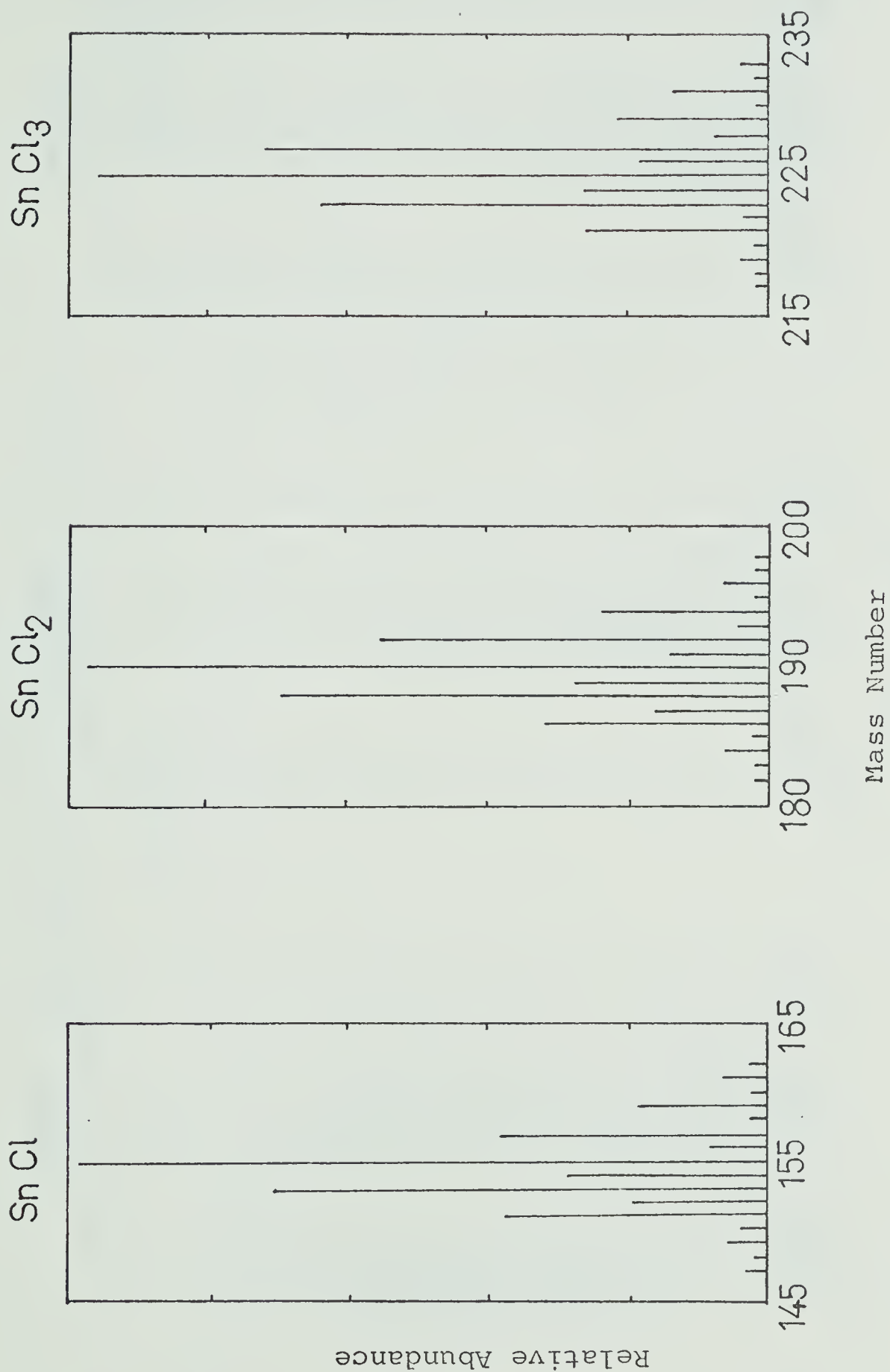


FIGURE 14. Isotope Combination Patterns for SnCl, SnCl₂ and SnCl₃.

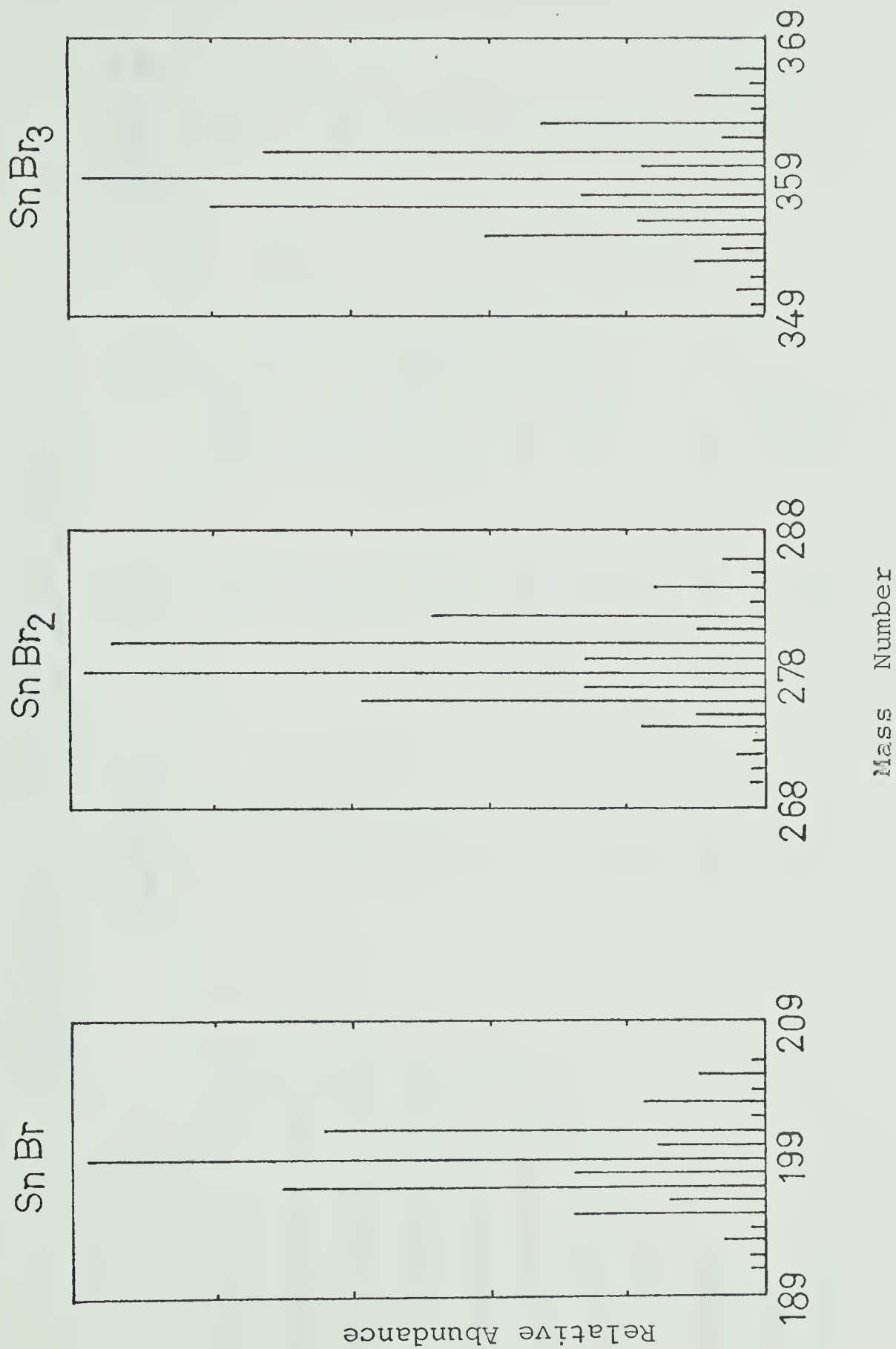


FIGURE 15. Isotope Combination Patterns for SnBr , SnBr_2 and SnBr_3 .

TABLE VII

Mass Spectrum of $\text{Me}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$

m/e^a	Ion	Relative abundance	m/e^a	Ion	Relative abundance
346	$\text{Me}_3\text{SnFe}(\text{CO})_3(\text{C}_3\text{H}_5)^+$	46	135	MeSn^+	280
331	$\text{Me}_2\text{SnFe}(\text{CO})_3(\text{C}_3\text{H}_5)^+$	19	125	$\text{Fe}(\text{CO})(\text{C}_3\text{H}_5)^+$	32
318	$\text{Me}_3\text{SnFe}(\text{CO})_2(\text{C}_3\text{H}_5)^+$	136	120	Sn^+	82
303	$\text{Me}_2\text{SnFe}(\text{CO})_2(\text{C}_3\text{H}_5)^+$	17	97	$\text{Fe}(\text{C}_3\text{H}_5)^+$	102
290	$\text{Me}_3\text{SnFe}(\text{CO})(\text{C}_3\text{H}_5)^+$	82	96	$\text{Fe}(\text{C}_3\text{H}_4)^+$	49
275	$\text{Me}_2\text{SnFe}(\text{CO})(\text{C}_3\text{H}_5)^+$	54	95	$\text{Me}(\text{C}_3\text{H}_3)^+$	63
262	$\text{Me}_3\text{SnFe}(\text{C}_3\text{H}_5)^+$	68	84	$\text{Fe}(\text{CO})^+$	28
206	Me_2SnFe^+	540	71		61
191	MeSnFe^+	100	56	Fe^+	79
176	SnFe^+	157	41	C_3H_5^+	33
165	Me_3Sn^+	480	39	C_3H_3^+	27

^a The m/e value given in this table is for the ion containing ^{120}Sn .

TABLE VIII

Mass Spectrum of $\text{Me}_2\text{ClGeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)^*$

m/e^a	Ion	Relative abundance	m/e^a	Ion	Relative abundance
	No parent ion	—	165	ClGeFe^+	12
305	$\text{MeClGeFe}(\text{CO})_3(\text{C}_3\text{H}_5)^+$	2	145 ^b	MeGeFe^+	27
292	$\text{Me}_2\text{ClGeFe}(\text{CO})_2(\text{C}_3\text{H}_5)^+$	17	139	Me_2GeCl^+	31
285	$\text{Me}_2\text{GeFe}(\text{CO})_3(\text{C}_3\text{H}_5)^+$	3	130	GeFe^+	7
277	$\text{MeClGeFe}(\text{CO})_2(\text{C}_3\text{H}_5)^+$	2	125	$\text{Fe}(\text{CO})(\text{C}_3\text{H}_5)^+$	10
264	$\text{Me}_2\text{ClGeFe}(\text{CO})(\text{C}_3\text{H}_5)^+$	62	115	$\text{Ge}(\text{C}_3\text{H}_5)^+$	21
257	$\text{Me}_2\text{GeFe}(\text{CO})_2(\text{C}_3\text{H}_5)^+$	6	105	Me_2GeH^+	11
249	$\text{MeClGeFe}(\text{CO})(\text{C}_3\text{H}_5)^+$	6	97	$\text{Fe}(\text{C}_3\text{H}_5)^+$	23
236	$\text{Me}_2\text{ClGeFe}(\text{C}_3\text{H}_5)^+$	133	95	$\text{Fe}(\text{C}_3\text{H}_3)^+$	14
229	$\text{Me}_2\text{GeFe}(\text{CO})(\text{C}_3\text{H}_5)^+$	8	89	MeGe^+	76
221	$\text{MeClGeFe}(\text{C}_3\text{H}_5)^+$	8	71		19
206	$\text{ClGeFe}(\text{C}_3\text{H}_5)^+$	2	56	Fe^+	45
195	$\text{Me}_2\text{ClGeFe}^+$	25	41	C_3H_5^+	18
180	MeClGeFe^+	100	39	C_3H_3^+	14

continued

*The expected isotope pattern for one germanium and one chlorine was observed.

^am/e values for ⁷⁴Ge and ³⁵Cl containing fragments.

^bAssignment is not certain owing to overlap with other series.

TABLE IX

Mass Spectrum of $\text{PhI}_2\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$

m/e^a	Ion	Relative abundance	m/e^a	Ion	Relative abundance
623	$\text{PhI}_2\text{SnFe}(\text{CO})_3(\text{C}_3\text{H}_5)^+$	7	183	IFe^+	92
604	$\text{PhI}_2\text{SnFe}(\text{CO})_2(\text{C}_3\text{H}_5)^+$	60	127	I^+	24
576	$\text{PhI}_2\text{SnFe}(\text{CO})(\text{C}_3\text{H}_5)^+$	230	125	$\text{Fe}(\text{CO})(\text{C}_3\text{H}_5)^+$	92
548	$\text{PhI}_2\text{SnFe}(\text{C}_3\text{H}_5)^+$	190	120	Sn^+	3000
507	$\text{PhI}_2\text{SnFe}^+$	70	97	$\text{Fe}(\text{C}_3\text{H}_5)^+$	260
451	PhI_2Sn^+	60	96	$\text{Fe}(\text{C}_3\text{H}_4)^+$	108
430	I_2SnFe^+	660	95	$\text{Fe}(\text{C}_3\text{H}_3)^+$	160
421	$\text{PhISnFe}(\text{C}_3\text{H}_5)^+$	40	84	$\text{Fe}(\text{CO})^+$	76
380	PhISnFe^+	100	78	C_6H_6^+	88
374	I_2Sn^+	22	77	C_6H_5^+	248
344	$\text{ISnFe}(\text{C}_3\text{H}_5)^+$	23	71		92
303	ISnFe^+	110	56	Fe^+	360
247	ISn^+	820	51	C_4H_3^+	300
224	$\text{IFe}(\text{C}_3\text{H}_5)^+$	68	41	C_3H_5^+	172
197	PhSn^+	1200	39	C_3H_3^+	273

^a m/e values for ^{120}Sn containing fragments.

TABLE X

Mass Spectrum of $\text{Br}_3\text{SnFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$

m/e	Ion	Relative abundance	m/e	Ion	Relative abundance
540*	$\text{Br}_3\text{SnFe}(\text{CO})_3(\text{C}_3\text{H}_5)^+$	1	178 ^b	$\text{BrFe}(\text{C}_3\text{H}_5)^+$	68
512*	$\text{Br}_3\text{SnFe}(\text{CO})_2(\text{C}_3\text{H}_5)^+$	18	166	$\text{Fe}(\text{CO})_2(\text{C}_4\text{H}_6)^+$	74
484*	$\text{Br}_3\text{SnFe}(\text{CO})(\text{C}_3\text{H}_5)^+$	10	153	$\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_5)^+$	2060
456*	$\text{Br}_3\text{SnFe}(\text{C}_3\text{H}_5)^+$	124	138	$\text{Fe}(\text{CO})(\text{C}_4\text{H}_6)^+$	158
415*	Br_3SnFe^+	42	137 ^b	BrFe^+	46
375**	$\text{Br}_2\text{SnFe}(\text{C}_3\text{H}_5)^+$	8	125	$\text{Fe}(\text{CO})(\text{C}_3\text{H}_5)^+$	1020
353 ^a		44	120	Sn^+	110
334**	Br_2SnFe^+	11	112	$\text{Fe}(\text{CO})_2^+$	210
319**	$\text{Br}_2\text{Sn}(\text{C}_3\text{H}_5)^+$	37	97	$\text{Fe}(\text{C}_3\text{H}_5)^+$	7200
278***	Br_2Sn^+	260	95	$\text{Fe}(\text{C}_3\text{H}_5)^+$	1630
262 ^b	$\text{BrFe}(\text{CO})_3(\text{C}_3\text{H}_5)^+$	12	84	$\text{Fe}(\text{CO})^+$	740
255**	BrSnFe^+	10	81	Br^+	228
234 ^b	$\text{BrFe}(\text{CO})_2(\text{C}_3\text{H}_5)^+$	42	71		1080
206 ^b	$\text{BrFe}(\text{CO})(\text{C}_3\text{H}_5)^+$	86	56	Fe^+	2240
199***	BrSn^+	700	41	C_3H_5^+	Off Scale

(continued)

TABLE X (continued)

m/e	Ion	Relative abundance	m/e	Ion	Relative abundance
181	$\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_5)^+$	660	39	C_3H_3^+	Off Scale

* The expected isotope pattern for one tin atom and three bromine atoms was observed for this ion. The m/e value given in this table is for the most abundant peak.

** The expected isotope pattern for one tin and two bromine was observed for this ion. The m/e value is for the most abundant peak.

a Complex isotope pattern different from one tin and three, two or one bromine pattern.

b m/e value for ^{81}Br containing fragment.

*** The expected isotope pattern was observed for one tin and one bromine. The m/e value is for the most abundant peak.

TABLE XI

Mass Spectrum of $\text{MeClSn}[\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)]_2$

m/e^a	Ion	Relative abundance	m/e^a	Ion	Relative abundance
532	$\text{MeClSnFe}_2(\text{CO})_6(\text{C}_3\text{H}_5)_2^+$	32	232 ^e	SnFe_2^+	460
517	$\text{ClSnFe}_2(\text{CO})_6(\text{C}_3\text{H}_5)_2^+$	1	226	MeClSnFe^+	640
504	$\text{MeClSnFe}_2(\text{CO})_5(\text{C}_3\text{H}_5)_2^+$	36	185	Me_2ClSn^+	3000
497	$\text{MeSnFe}_2(\text{CO})_6(\text{C}_3\text{H}_5)_2^+$	16	176	SnFe^+	840
489	$\text{ClSnFe}_2(\text{CO})_5(\text{C}_3\text{H}_5)_2^+$	6	161	$\text{Sn}(\text{C}_3\text{H}_5)^+$	2600
476	$\text{MeClSnFe}_2(\text{CO})_4(\text{C}_3\text{H}_5)_2^+$	26	155	ClSn^+	1420
469	$\text{MeSnFe}_2(\text{CO})_5(\text{C}_3\text{H}_5)_2^+$	8	138	$\text{Fe}(\text{CO})(\text{C}_4\text{H}_6)^+$	5200
448	$\text{MeClSnFe}_2(\text{CO})_3(\text{C}_3\text{H}_5)_2^+$	100	135	MeSn^+	1680
433	$\text{ClSnFe}_2(\text{CO})_3(\text{C}_3\text{H}_5)_2^+$	30	125	$\text{Fe}(\text{CO})(\text{C}_3\text{H}_5)^+$	2400
420	$\text{MeClSnFe}_2(\text{CO})_2(\text{C}_3\text{H}_5)_2^+$	102	120	Sn^+	980
392	$\text{MeClSnFe}_2(\text{CO})(\text{C}_3\text{H}_5)_2^+$	126	97	$\text{Fe}(\text{C}_3\text{H}_5)^+$	6400
379	$\text{MeClSnFe}_2(\text{CO})_2(\text{C}_3\text{H}_5)^+$	30	96	$\text{Fe}(\text{C}_3\text{H}_4)^+$	4800
364	$\text{MeClSnFe}_2(\text{C}_3\text{H}_5)_2^+$	560	95	$\text{Fe}(\text{C}_3\text{H}_3)^+$	4600
351	$\text{MeClSnFe}_2(\text{CO})(\text{C}_3\text{H}_5)^+$	1120	84	$\text{Fe}(\text{CO})^+$	1420

continued

TABLE XI (continued)

m/e ^a	Ion	Relative abundance	m/e ^a	Ion	Relative abundance
323	MeClSnFe ₂ (C ₃ H ₅) ⁺	540	71		3000
310 ^b	MeClSnFe ₂ (CO) ⁺	240	67	C ₅ H ₇ ⁺	3400
308 ^b	ClSnFe ₂ (C ₃ H ₅) ⁺	320	56	Fe ⁺	10000
302 ^c		460	54	C ₄ H ₆ ⁺	1420
295	ClSnFe ₂ (CO) ⁺	400	41	C ₃ H ₅ ⁺	13200
275 ^b	MeSnFe ₂ (CO) ⁺	1040	40	C ₃ H ₄ ⁺	5600
273 ^b	SnFe ₂ (C ₃ H ₅) ⁺	1020	39	C ₃ H ₃ ⁺	16800
267 ^d	ClSnFe ₂ ⁺	1220			

* The expected isotope pattern for one tin and one chlorine was observed.

a m/e values for ¹²⁰Sn- and ³⁵Cl-containing fragments

b Assignment is not certain owing to overlap with fragments of other series.

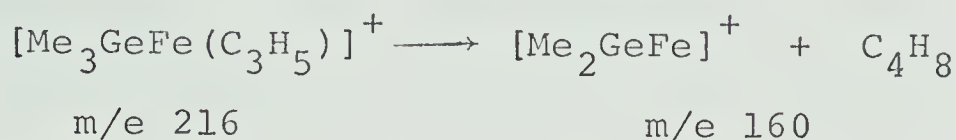
c Sn pattern.

d Overlapped with MeClSnFe(C₃H₅)⁺.

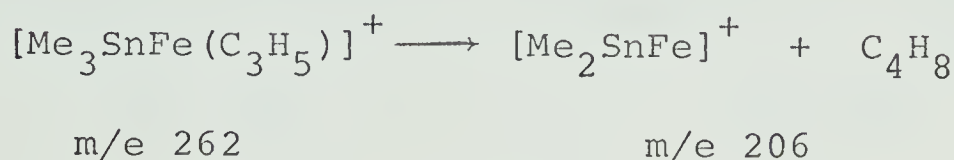
e Overlapped with MeSnFe(C₃H₅)⁺.

not observed.

The ion $[\text{Me}_3\text{MFe}(\text{C}_3\text{H}_5)]^+$ lost allyl and methyl groups to give a very abundant ion $[\text{Me}_2\text{MFe}]^+$.



metastable ion at m/e 118.5 ($160^2/216 = 118.5$)

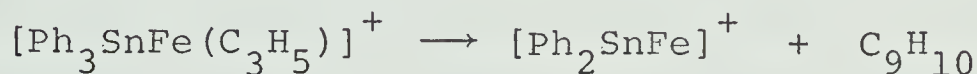


metastable ion at m/e 161.8 ($206^2/262 = 161.9$)

This may present an interesting feature of the present system as compared with π -cyclopentadienyl derivatives in which all methyl groups are lost before losing the cyclopentadienyl ring. This feature was more pronounced if M carried phenyl groups and/or halogens.

The mass spectra of various germanium derivatives in which the germanium atom bonded both methyl (or phenyl) groups and halogens at the same time did not show molecular ions. The mass spectra of $\text{Me}_n\text{Cl}_{3-n}\text{GeFe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$ ($n = 1, 2$) possessed fragments due to $[\text{Me}_n\text{Cl}_{3-n}\text{GeFe}(\text{CO})_x(\text{C}_3\text{H}_5)]^+$ ($x = 2, 1, 0$) as well as fragments due to loss of one methyl or one chlorine. The $[\text{Me}_n\text{Cl}_{3-n}\text{GeFe}(\text{C}_3\text{H}_5)]^+$ ion again lost a neutral fragment, C_4H_8 , to give very abundant ion, $[\text{Me}_{n-1}\text{Cl}_{3-n}\text{GeFe}]^+$.

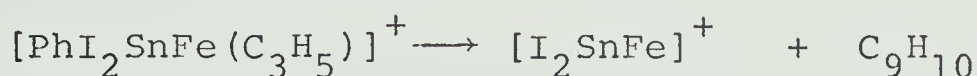
In the phenyl halogenotin or germanium derivatives, a C_9H_{10} fragment (probably allylbenzene) was lost from the ion $[Ph_nX_{3-n}MFe(C_3H_5)]^+$. For example $[Ph_3SnFe(C_3H_5)]^+$, $[PhI_2SnFe(C_3H_5)]^+$, and $[Ph_2ClGeFe(C_3H_5)]^+$ gave very abundant ions, $[Ph_2SnFe]^+$, $[I_2SnFe]^+$, and $[PhClGeFe]^+$ respectively.



m/e 448

m/e 330

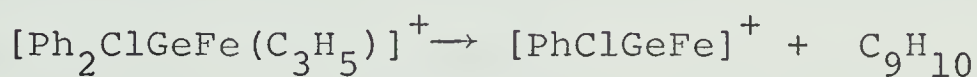
metastable ion at m/e 243.1 ($330^2/448 = 243.08$)



m/e 548

m/e 430

metastable ion at m/e 337.4 ($430^2/548 = 337.4$)



m/e 360

m/e 242

metastable ion at m/e 162.5 ($242^2/360 = 162.6$)

On the other hand, the corresponding fragmentation pathway in which the ion $[R_nX_{3-n}MFe(C_3H_5)]^+$ lose an allyl halide (C_3H_5X) to give the $[R_nX_{2-n}MFe]^+$ was not certain because a metastable ion corresponding to this fragmentation could not be observed, although the latter ion could be seen.

The mass spectra of bis(π -allyltricarboxyliron) derivatives possessed fragments due to stepwise loss of six

carbonyl groups from the parent ion. The most interesting feature of the mass spectra of this series was that one of the allyl groups was lost before loss of carbonyl groups was complete. However, the number of the carbonyl groups on the ion which had lost its first allyl group depended upon compounds. In most cases, three or four carbonyl groups had been lost before losing an allyl group. In this series, the comparable loss of a methyl, a halogen and a carbonyl group from the molecular ion was also observed. The bare metal pairs, $[\text{SnFe}_2]^+$, $[\text{SnFe}]^+$ were observed in moderate to high abundance.

EXPERIMENTAL

Infrared spectra were measured with a Perkin-Elmer 337 grating spectrometer and recorded in expanded form on a Hewlett-Packard 7127A recorder.

All spectra were measured in spectroscopic grade cyclohexane solution at a concentration of 1-2 mg./ml. using 0.5 mm KBr or KCl cells, and calibrated using a carbon monoxide gas cell.

The nuclear magnetic resonance spectra were measured on a Varian A56/60 and HA 100 spectrometer, using tetramethylsilane as an internal reference. All the compounds described in this chapter gave sharp NMR resonances and are thus presumed to be diamagnetic. In the studies of temperature effects, the temperature of the sample was controlled

by the attached temperature controller. Temperatures below machine temperature were obtained by the use of liquid nitrogen.

Mass spectra were taken with Associated Electrical Industries MS-9 and MS-12 instruments, using direct introduction of solid sample. Normally source temperatures of below 100° were employed.

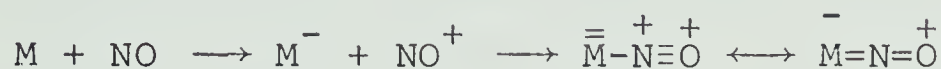
CHAPTER IVTransition Metal Nitrosyl DerivativesINTRODUCTION

Since this Chapter and most part of Chapter V describe transition metal nitrosyls, a brief discussion of these compounds is presented here. Metal nitrosyls have been reviewed by Johnson and McCleverty (101), and more recently by Griffith (102).

Nitric oxide (NO), like carbon monoxide, forms bonds to transition metals. However, NO has an additional electron in an antibonding molecular orbital which is fairly easily lost (the ionization potential of NO is 9.5 eV) to give the nitrosonium ion, NO^+ . The NO^+ ion (isoelectronic with CO), therefore, should have a stronger N-O bond than NO itself. This is confirmed by NO stretching frequencies of 2400 - 2150 cm^{-1} in NO^+ salts, as compared to 1840 cm^{-1} in free NO (103), and also by the shorter N-O bond length in NO^+ as compared with NO (1.062 Å vs. 1.151 Å) (102).

The majority of transition metal nitrosyls may be regarded in a formal sense as being formed by the initial transfer of the antibonding electron from NO to the metal atom, reducing its oxidation state by one unit, followed by donation of an electron pair from the resultant NO^+ to the metal atom with metal-nitrogen back donation in a manner

entirely analogous to that in the metal-carbon in carbonyl compounds.



Thus three electrons are involved in the metal-nitrosyl bond and NO can formally be regarded as a three-electron donor. With this assumption, nitrosyl compounds very often satisfy the effective atomic number rule.

There is ample evidence for metal-nitrogen back bonding. A terminal NO stretching frequency in the range 1950-1450 cm^{-1} suggests that the NO group has a very substantial π -acceptor capacity, probably greater than that of CO group, since the lowering of the stretching frequency upon coordination is greater. It should also be noted that the CO group is always replaced in the reaction of carbonyl-nitrosyl compounds such as $\text{Mn}(\text{CO})_4\text{NO}$ and $\text{Co}(\text{CO})_3\text{NO}$ with various nucleophiles such as phosphines (104,105).

There are other types of nitrosyl compounds, where the NO molecule may be considered to contribute either one or two electrons to the metal-nitrosyl bond. For example, the complexes, $[\text{Co}(\text{NH}_3)_5\text{NO}]^{++}$ and $[\text{Co}(\text{CN})_5\text{NO}]^{3-}$ have generally been considered to contain NO^- . In these complexes, the transfer of an electron from cobalt to NO, giving NO^- , has been postulated. The NO^- ion would behave as an ordinary anionic ligand, donating an electron pair (106).

Finally, in $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ ion, though not yet isolated, and the nitrosyl complex formed by heme, the antibonding electron resides mainly in an NO molecular orbital. Thus the outer electron configuration would be $(d_{xz}, d_{yz})^4 d_{xy}^2 (\pi^* \text{NO})^1$. Evidence for this has been obtained from ESR data (106,107). The formation of nitrosyl compounds of the latter two types is so limited that such compounds will not be discussed further.

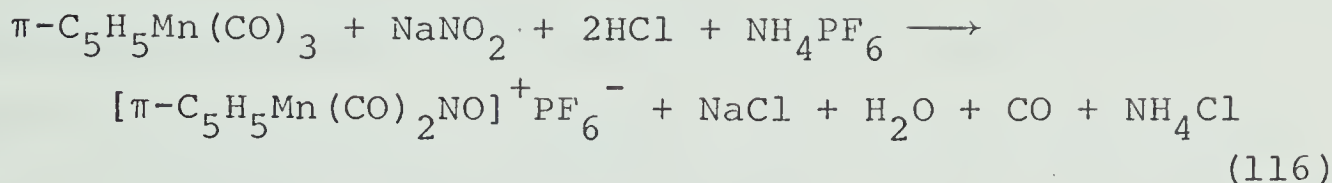
Transition metal nitrosyl compounds have been prepared by the following methods.

(i) Reaction of metal carbonyls or their derivatives with nitric oxide:



This method is the most generally applicable. Representative compounds which have been obtained by this method (with starting material in square brackets) are $\text{Fe}(\text{CO})_2(\text{NO})_2$ [$\text{Fe}_3(\text{CO})_{12}$, $\text{Fe}_2(\text{CO})_9$, $\text{Fe}(\text{CO})_5$] (109), $\text{V}(\text{CO})_5\text{NO}$ [$\text{V}(\text{CO})_6$] (110), $\text{Mn}(\text{CO})_4\text{NO}$ [$\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$] (111), $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2\text{NO}$ [$(\pi\text{-C}_5\text{H}_5)_2\text{M}_2^-(\text{CO})_6$, where $\text{M} = \text{Cr}$ (112), Mo (113), W (114)]. Further reaction of $\text{Mn}(\text{CO})_4\text{NO}$ with NO gives $\text{Mn}(\text{CO})(\text{NO})_3$ (111). Upon irradiation of $\text{Mn}(\text{CO})_4\text{NO}$ with ultraviolet light, $\text{Mn}_2(\text{CO})_7^-(\text{NO})_2$ is obtained (115); its structure presumably analogous to $\text{Fe}_2(\text{CO})_9$.

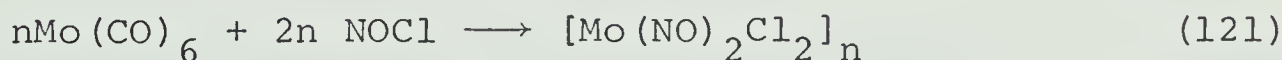
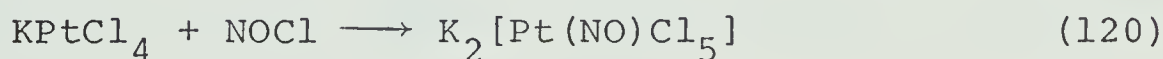
(ii) Reaction of metal carbonyls or their derivatives with nitrite ion:



Treatment of an aqueous suspension of $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}]^+\text{PF}_6^-$ with aqueous NaBH_4 gives the dimeric nitrosyl derivative, $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})(\text{NO})]_2$ (117), whose benzene solution gives $(\pi\text{-C}_5\text{H}_5)_3\text{Mn}_3(\text{NO})_4$ upon irradiation with ultraviolet light (118). The latter two compounds have bridging nitrosyl groups.

Reaction of $\text{Fe}(\text{CO})_5$ with nitrite ion in methanol produces $\text{Fe}(\text{CO})_3\text{NO}^-$ (119), which can be isolated as a mercury salt, $\text{Hg}[\text{Fe}(\text{CO})_3\text{NO}]_2$. The anion can be better prepared in the presence of a base such as NaOH or MeONa (119).

(iii) Reaction of metal salts or metal carbonyls with nitrosyl halides:

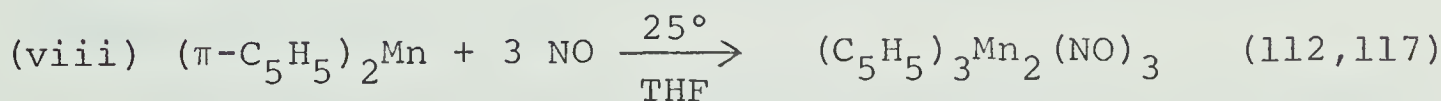
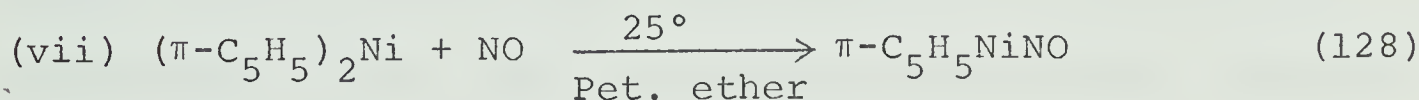
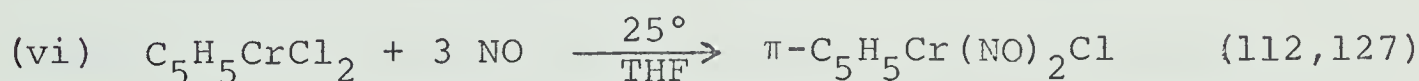
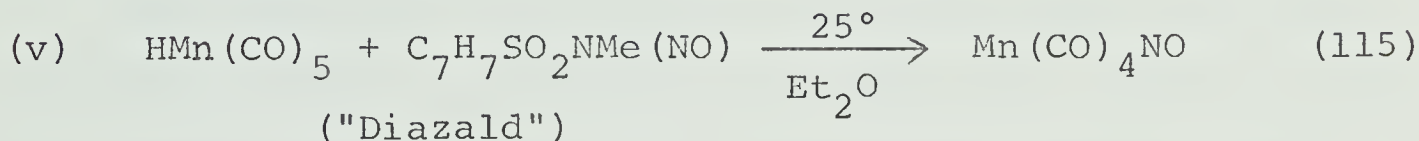


The mono- or dinitrosyl metal derivatives prepared in this way are mainly polymeric with halogen bridges, and react with additional donor molecules such as phosphines, phosphites, and amines to give monomeric derivatives. These nitrosyl metal halides are formed especially by Fe, Co, Ni, V, Mn, Mo, W, Pd, Pt, Os, Rh, Ir and Cu (122). It is noteworthy that $[\text{Mo}(\text{NO})_2\text{Cl}_2]_n$ reacts with thallium cyclopentadienide to give unstable $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{NO})_2\text{Cl}$ (123).

Similarly, treatment of $[\text{Pd}(\text{NO})\text{Cl}]_n$ with sodium cyclopentadienide produces $\pi\text{-C}_5\text{H}_5\text{PdNO}$ (124), while the corresponding platinum compound, $\pi\text{-C}_5\text{H}_5\text{PtNO}$, can be obtained from $\text{Pt}_2(\text{CO})_2\text{Cl}_4$, sodium cyclopentadienide and NO (125).

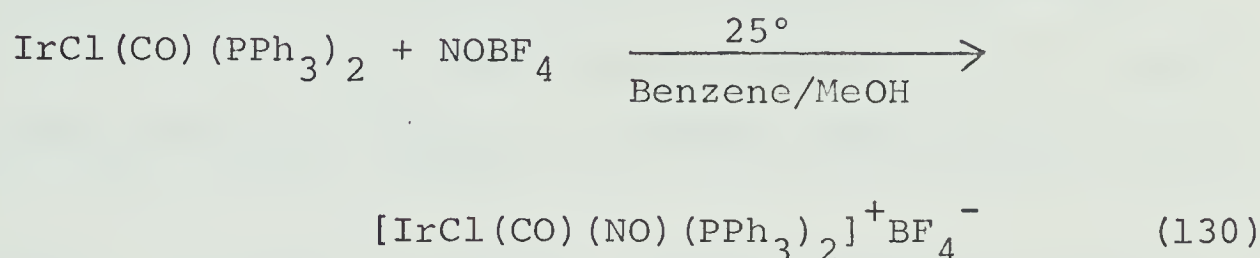
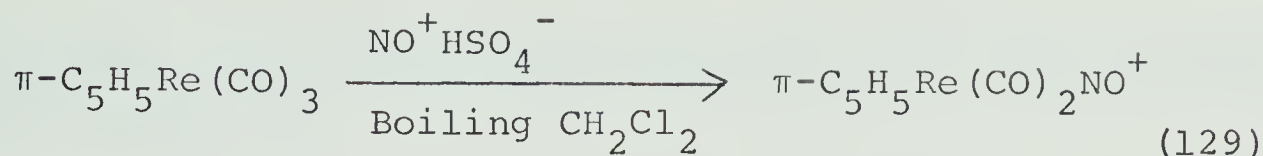
(iv) Reaction of hexacyano complexes with hydroxylamine hydrochloride in base or with nitric acid; these are mostly of the type $[\text{M}(\text{NO})(\text{CN})_3]^{n-}$, and spectroscopic studies of these compounds indicate that there is very strong M-NO π -bonding (126), certainly greater than M-CO π -bonding in metal carbonyl anions.

In a few instances, special methods are available, as shown in the following reactions.



Although the formalism in which carbonyl nitrosyls are considered to involve coordinated NO^+ is widely used, the actual use of NO^+ as a reagent with metal carbonyls has been largely unexplored. The only reported examples of such reactions prior to the beginning of the present work were

the following reactions.



Very recently Pierpont et al. reported a compound, $[\text{RuCl(NO)}_2(\text{PPh}_3)_2]^+\text{PF}_6^-$, prepared by a similar method used to obtain the Iridium compound (131).

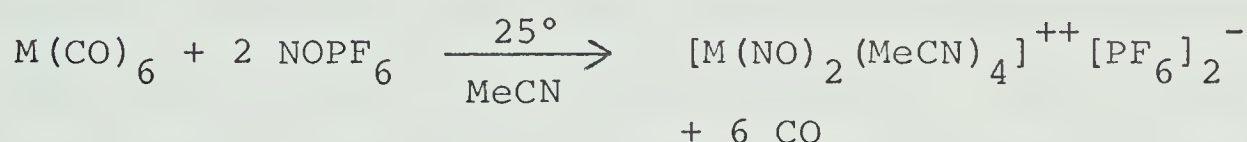
The commercial availability of nitrosonium salts such as NOBF_4 and NOPF_6 prompted us to undertake a general study of nitrosonium ion reactions. After this work was well advanced, we learned that nitrosonium cation reactions with metal carbonyls were being investigated at the University of Wisconsin by Dr. Neil G. Connelly and Professor Lawrence F. Dahl, who have since published a communication outlining their work (132).

This Chapter describes efforts directed to the systematic preparation of nitrosyl compounds of the chromium, molybdenum and tungsten series by the employment of NOPF_6 (Part A). In Part B, various reactions of other carbonyls and their derivatives with NOPF_6 are discussed.

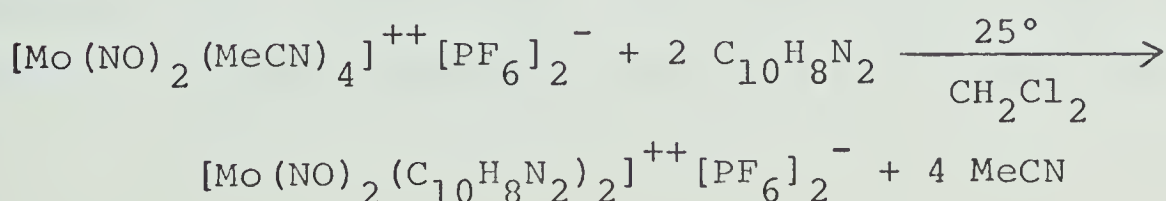
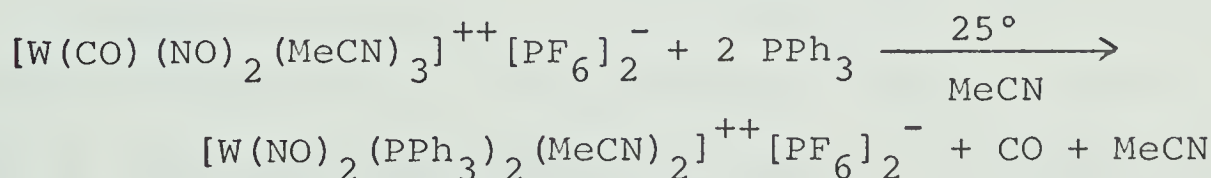
RESULTS AND DISCUSSION

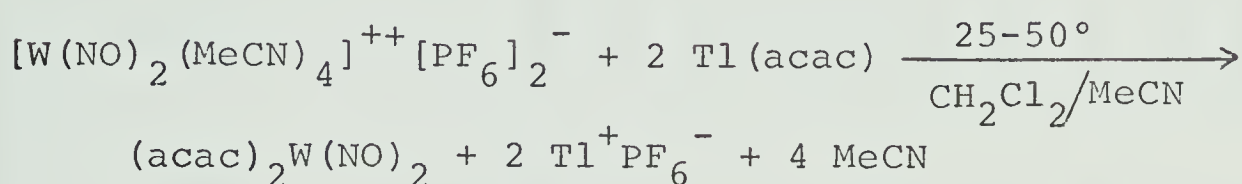
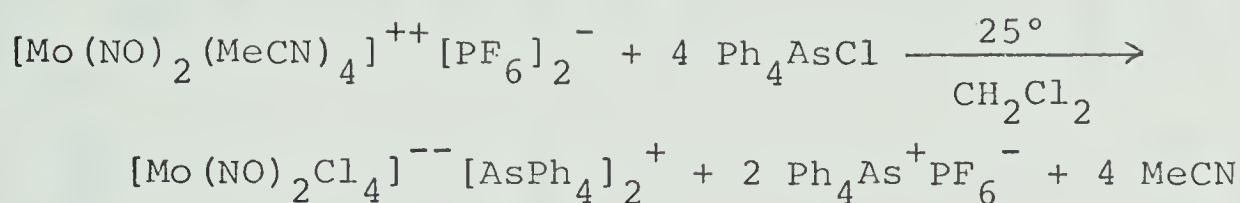
A. Nitrosyl compounds derived from $M(\text{CO})_6$ and NOPF_6 , (where $M = \text{Cr}, \text{Mo}, \text{W}$).

It was found that NOPF_6 reacts readily with $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) at room temperature in acetonitrile to produce $[\text{M}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ in almost quantitative yield.



Interestingly, when the reaction mixture was worked up quickly, $\text{W}(\text{CO})_6$ also gave a carbonyl-nitrosyl derivative, $[\text{W}(\text{CO})(\text{NO})_2(\text{MeCN})_3]^{++}[\text{PF}_6]_2^-$, in which the carbonyl group is quite labile. These compounds are brown to deep-green crystalline substances which are soluble in polar solvents such as MeCN, MeOH and EtOH, and insoluble in non-polar solvents. They react with additional ligands, such as phosphines, amines, Cl^- and acetylacetonate anion, to give either ionic or neutral nitrosyl derivatives. Typical reactions are:





All the compounds prepared in this work analyzed as the dinitrosyl derivatives, and mass spectral results established this conclusively for the neutral compounds. These compounds were air-stable, crystalline substances not substantially decomposed thermally below 100°; the ionic species were moisture sensitive. Table XII lists microanalytical data, together with melting points and colors.

With two exceptions, $[\text{Cr}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ and $[\text{Cr}(\text{NO})_2(\text{dipy})_2]^{++}[\text{PF}_6]_2^-$, the infrared spectra of these compounds exhibited two strong bands in the NO stretching region, thus indicating that the NO groups were in cis positions. Furthermore, extensive M-NO back bonding would account for the overall range ($\sim 1870 - \sim 1650 \text{ cm}^{-1}$) of NO frequencies (see Table XIII).

It should, however, be mentioned that the infrared spectral behavior of $[\text{M}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ (where M = Mo, W) and $[\text{W}(\text{CO})(\text{NO})_2(\text{MeCN})_3]^{++}[\text{PF}_6]_2^-$ in acetonitrile was somewhat more complicated. The positions of both bands shifted to lower wavenumber by 24-33 cm^{-1} with time. For

TABLE XII

Analytical Data, Colors and Melting Points for Nitrosyl Compounds of Cr, Mo, and W.*

Compound	M.P. (°C)	Color	Calcd %			Found %		
			C	H	N	C	H	N
(acac) ₂ Mo(NO) ₂ ^a	147	Green	33.91	3.98	7.91	33.84	3.93	7.89
(acac) ₂ W(NO) ₂	155	Green	27.17	3.19	6.34	27.48	3.21	6.51
(tfac) ₂ Mo(NO) ₂ ^b	123-132	Green	25.99	1.75	6.06	25.26	2.08	5.37
(tfac) ₂ W(NO) ₂	125-136	Green	21.84	1.47	5.09	21.76	2.04	4.88
(hfac) ₂ Mo(NO) ₂ ^c	52	Green	21.07	0.35	4.91	20.85	0.46	4.85
(hfac) ₂ W(NO) ₂	57	Brown	18.25	0.31	4.26	18.25	0.58	4.26
[Cr(NO) ₂ (MeCN) ₄] ⁺⁺ [PF ₆] ₂ ^{- d}	--	Brown	16.97	2.14	14.85	20.32	2.40	14.89
[Mo(NO) ₂ (MeCN) ₄] ⁺⁺ [PF ₆] ₂ ^{- e}	--	Green	15.75	1.98	13.77	15.62	2.05	13.56
[W(NO) ₂ (MeCN) ₄] ⁺⁺ [PF ₆] ₂ ^{- f}	--	Green	13.77	1.73	12.04	14.02	1.71	11.42
[W(CO)(NO) ₂ (MeCN) ₄] ⁺⁺ [PF ₆] ₂ ⁻	--	Green	12.27	1.32	10.22	12.12	1.79	9.90
[Cr(NO) ₂ (dipy) ₂] ⁺⁺ [PF ₆] ₂ ^{- g}	--	Green	33.63	2.26	11.77	34.30	2.59	11.56
[Mo(NO) ₂ (dipy) ₂] ⁺⁺ [PF ₆] ₂ ⁻	--	Green	31.68	2.13	11.08	31.76	2.12	10.78
[W(NO) ₂ (dipy) ₂] ⁺⁺ [PF ₆] ₂ ⁻	--	Green	28.39	1.91	9.93	28.88	1.90	9.63
[W(NO) ₂ (PPh ₃) ₂ (MeCN) ₂] ⁺⁺ [PF ₆] ₂ ^{- h}	--	Pale brown	42.13	3.18	4.91	42.49	3.41	5.65
[Cr(NO) ₂ (diphos) ₂] ⁺⁺ [PF ₆] ₂ ^{- i}	--	Orange	52.10	4.04	2.34	53.59	4.19	2.10

continued

- * Melting points for ionic species are not given because these compounds have only unsharp decomposition range.
- a acac = $\text{CH}_3\text{COCHCOCH}_3$
- b tfac = $\text{CF}_3\text{COCHCOCH}_3$
- c hfac = $\text{CF}_3\text{COCHCOCF}_3$
- d Calcd: Cr, 9.18; P, 10.94. Found: Cr, 9.43; P, 10.73. Repeated carbon analyses gave values between 20 and 21%.
- e Calcd: Mo, 15.73; P, 10.15. Found: Mo, 15.47; P, 10.01.
- f Calcd: W, 26.34; P, 8.88. Found: W, 27.62; P, 9.34.
- g dipy = 2,2'-dipyridyl.
- h PPh_3 = triphenylphosphine.
- i diphos = bis(1,2-diphenylphosphinoethane).

TABLE XIII

Infrared Spectra of Dinitrosyl Derivatives of Cr, Mo, and W.

Compound	Solvent	$\nu(\text{NO}), \text{cm}^{-1}$
(acac) ₂ Mo(NO) ₂ ^a	cyclohexane	1781 1670
(acac) ₂ W(NO) ₂	cyclohexane	1753 1652
(tfac) ₂ Mo(NO) ₂ ^b	cyclohexane	1800 1693
(tfac) ₂ W(NO) ₂	cyclohexane	1768 1674
(hfac) ₂ Mo(NO) ₂ ^c	cyclohexane	1825 1727
(hfac) ₂ W(NO) ₂	cyclohexane	1786 1697
[Cr(NO) ₂ (MeCN) ₄] ⁺⁺ [PF ₆] ₂ ⁻	MeCN	1790
[Mo(NO) ₂ (MeCN) ₄] ⁺⁺ [PF ₆] ₂ ⁻	nujol	1865 1770(sh) 1745
[W(NO) ₂ (MeCN) ₄] ⁺⁺ [PF ₆] ₂ ⁻	nujol	1835 1759(sh) 1722
[W(CO)(NO) ₂ (MeCN) ₃] ⁺⁺ [PF ₆] ₂ ^{-d}	nujol	1868 1778(sh) 1770
[Cr(NO) ₂ (dipy) ₂] ⁺⁺ [PF ₆] ₂ ^{-e}	MeCN	1764(sh) 1741
[Mo(NO) ₂ (dipy) ₂] ⁺⁺ [PF ₆] ₂ ⁻	MeCN	1827 1727
[W(NO) ₂ (dipy) ₂] ⁺⁺ [PF ₆] ₂ ⁻	MeCN	1792 1700
[W(NO) ₂ (PPh ₃) ₂ (MeCN) ₂] ⁺⁺ [PF ₆] ₂ ⁻	CH ₂ Cl ₂	1735 1660
[Cr(NO) ₂ (diphos) ₂] ⁺⁺ [PF ₆] ₂ ^{-f}	MeCN	1702 1667

continued

^a acac = $\text{CH}_3\text{COCHCOCH}_3$,

^b tfac = $\text{CF}_3\text{COCHCOCH}_3$

^c hfac = $\text{CF}_3\text{COCHCOCF}_3$

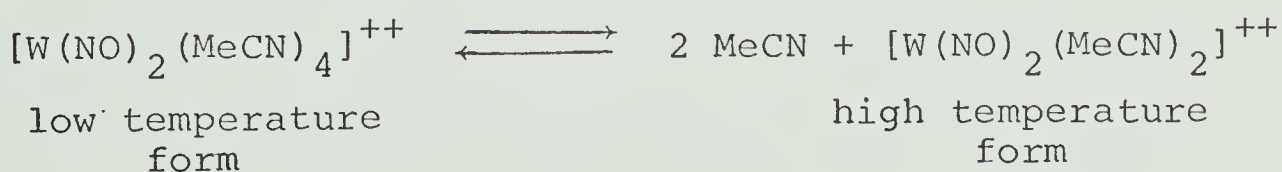
^d A strong $\nu(\text{CO})$ at 2164 cm^{-1} .

^e dipy = 2,2'-dipyridyl

^f diphos = bis(1,2-diphenylphosphinoethane).

example, a fresh acetonitrile solution of $[\text{W}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ showed bands at 1825 and 1730 cm^{-1} , and as these bands decreased in intensity, new bands at 1801 and 1700 cm^{-1} increased in intensity. After about 60 minutes, the initial bands had virtually disappeared.

NMR spectra of these compounds also changed with time. The proton spectrum of a fresh CD_3CN solution of $[\text{W}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ exhibited a sharp singlet at τ 7.4 due to the coordinated MeCN, which rapidly exchanged with CD_3CN and again after about 60 minutes, completely disappeared (at this stage a sharp singlet at τ 8.05 due to free MeCN was observed). A methylene chloride solution (prepared by stirring a suspension for 15 hours at room temperature) exhibited four NO stretching bands with almost the same intensities (1825, 1801, 1730 and 1700 cm^{-1}) in the infrared spectrum and two sharp singlets (τ 7.4 and 8.05) due to the coordinated and free MeCN in the proton spectrum (see Figure 16). An unproven but likely explanation for this is the formation of a species of lower coordination - most probably a four coordinate species with two MeCN groups, which might exist in equilibrium with the six coordinate species, considering that the aged acetonitrile solution gives the $[\text{W}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ by cooling to -80° .



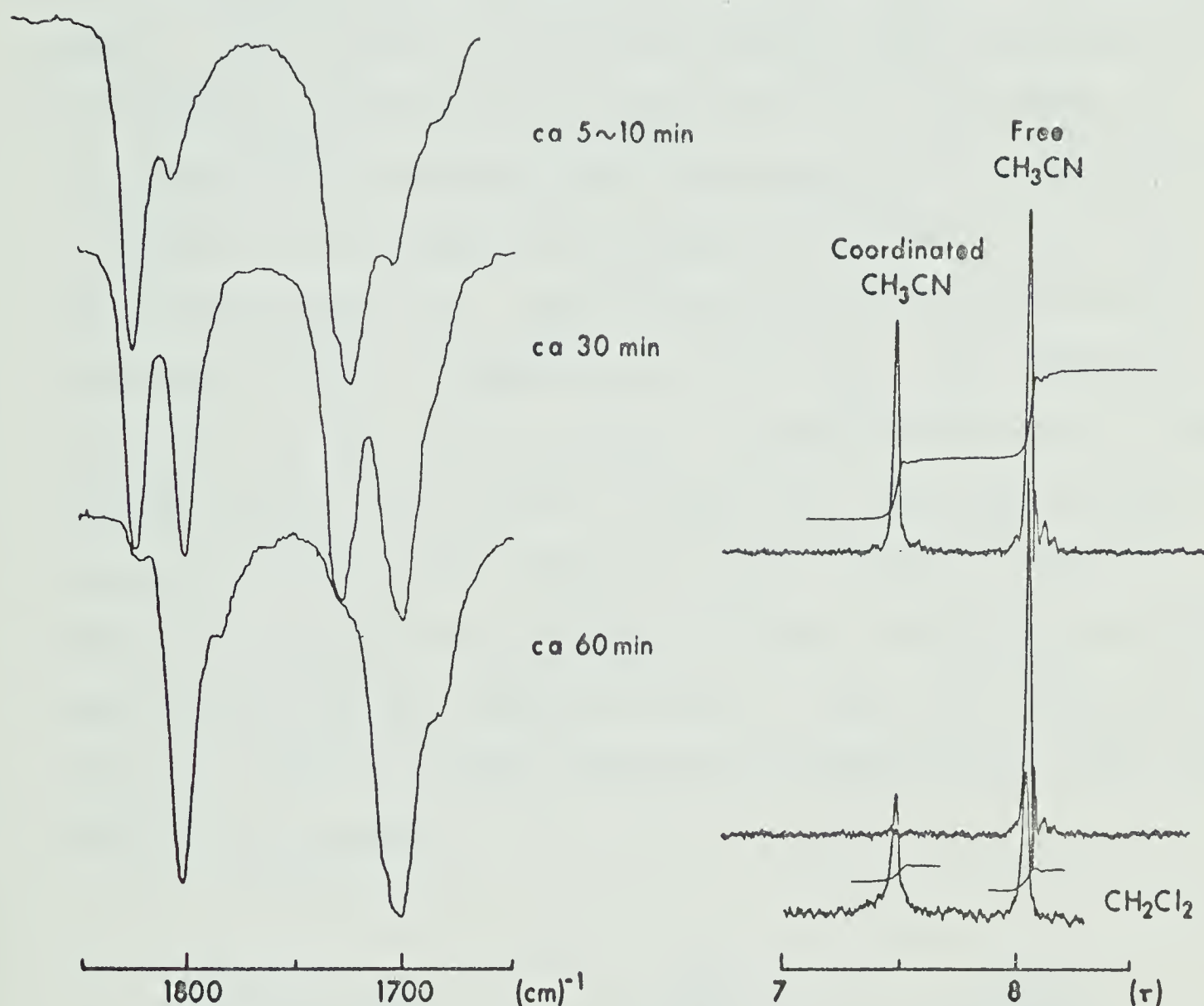
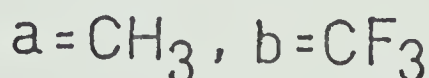
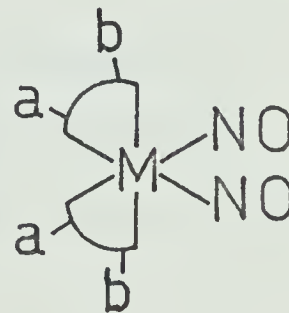
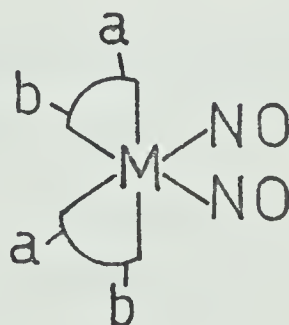
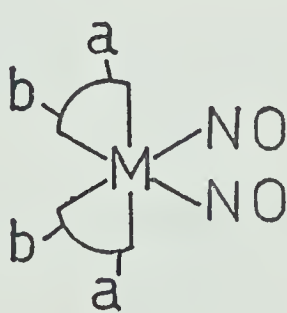


FIGURE 16. The infrared and proton NMR spectral changes with the lapse of time. The NMR spectrum at the bottom in CH_2Cl_2 did not undergo any further change.

Attempts to isolate the "four coordinate" cation as PtCl_4^{--} or PtCl_6^{--} salts were unsuccessful.

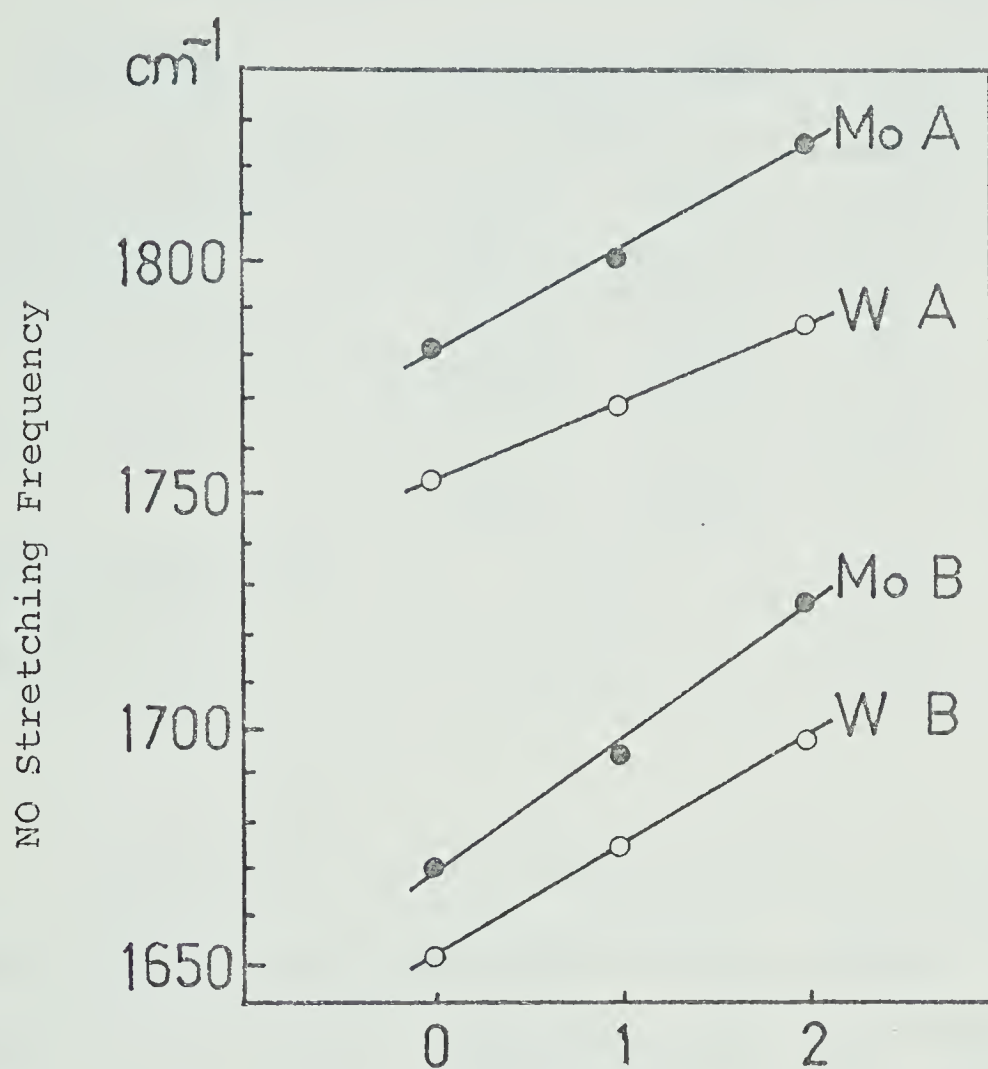
The reaction between the compounds and thallium(I) β -diketonates produced neutral derivatives, such as $(\text{acac})_2\text{W}(\text{NO})_2$, $(\text{tfac})_2\text{W}(\text{NO})_2$, and $(\text{hfac})_2\text{W}(\text{NO})_2$. The variation of NO stretching frequencies in this series as the number of CF_3 group in the chelate ring increases, may be interpreted in terms of the strong σ -withdrawing character of the CF_3 group (see Figure 17). The NMR spectra are of particular importance in the assignment of structures. The chemical shifts of the CH_3 and CF_3 groups, together with those of the methine proton, are listed in Table XIV. The most obvious implication of the NMR spectra is that in all of these β -diketone compounds the β -diketone groups occupy cis positions, consistent with the infrared result. Thus, for $(\text{tfac})_2\text{M}(\text{NO})_2$ (where $\text{M} = \text{Mo}, \text{W}$), three geometrical isomers XXVI, XXVII and XXVIII are possible.



XXVI

XXVII

XXVIII



Number of CF₃ groups in β-diketone group.

FIGURE 17. The NO stretching frequency versus the number of CF₃ group for the β-diketone compounds. A denotes A mode, and B denotes B mode of NO stretching.

TABLE XIV

NMR Data for β -diketone Compounds ^a

Compound	¹ H ^b			¹⁹ F ^c	
	CH ₃		-CH-	CF ₃	
(acac) ₂ Mo(NO) ₂ ^d	7.80	8.02	4.39	-----	
(acac) ₂ W(NO) ₂	7.76	7.99	4.31	-----	
(tfac) ₂ Mo(NO) ₂ ^e	7.57	7.58	3.92	74.06	74.13
	7.79	7.81		74.83	74.91
(tfac) ₂ W(NO) ₂	7.53	7.54	3.86	74.10	74.15
	7.77	7.79		74.99	75.05
(hfac) ₂ Mo(NO) ₂ ^f	-----		3.48	74.72	75.48
(hfac) ₂ W(NO) ₂	-----		3.40	74.67	75.53

^a

All spectra were measured on Varian A56/60 instrument.

Solvent was CDCl₃. Temperature 30° (¹H, ¹⁹F). Concentration was about 0.2 M.^b

Proton shifts are in ppm relative to TMS (1% by volume)

^cFluorine shifts are in ppm relative to an external reference of CFCl₃.^dacac = CH₃COCHCOCH₃.^etfac = CF₃COCHCOCH₃.^fhfac = CF₃COCHCOCF₃.

The observed NMR spectra for $(\text{tfac})_2\text{W}(\text{NO})_2$ is shown in Figure 18. The spectrum at the top in Figure 18 shows the ^{19}F (CF_3) resonances, while the proton spectrum at the bottom including expanded forms was measured at 100 Mc. in benzene- d_6 in order to take advantage of the large possible diamagnetic anisotropy effect on β -diketonates in this solvent (133, 134). The spectrum represented a large improvement over that obtained using CDCl_3 as solvent. The two resonance lines of the equal intermediate intensity should correspond to XXVII and therefore the rest are due to XXVI and XXVIII. One configuration, either XXVI or XXVIII was preferred over other configurations, and the total amount of XXVI and XXVIII was found to be exactly equal to that of XXVII on the basis of relative integrated intensities of both CH_3 and CF_3 resonances (XXVII : (XXVI, XXVIII) = 32 : (11,21)).

Finally it is noteworthy that none of the β -diketone derivatives described undergoes exchange of CH_3 or CF_3 groups between the two nonequivalent sites of the cis isomer, even at elevated temperatures. Furthermore, they are remarkably substitution-inert to free β -diketones, even activated compounds such as hexafluoroacetylacetone. This is the most striking characteristic of these compounds, considering that the β -diketone group in many known bis(β -diketone) derivatives of transition metals is labile (134,135).

The mass spectra of β -diketone compounds of molybdenum

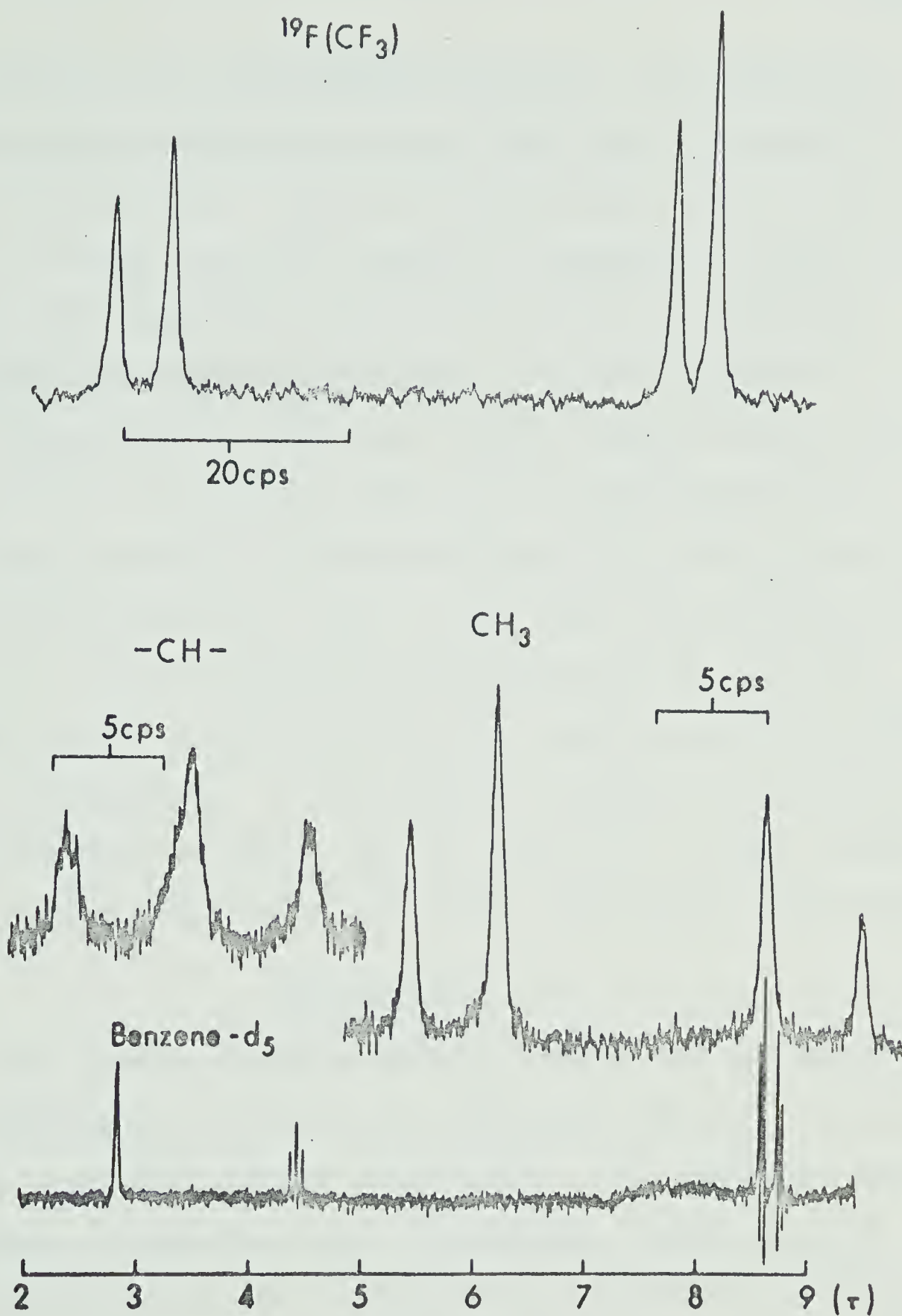


FIGURE 18. The NMR spectra of $(\text{tfac})_2\text{W}(\text{NO})_2$. The top spectrum is ^{19}F resonances and the bottom spectrum with expanded forms is ^1H resonances.

and tungsten are summarized in Table XV. All exhibited a very strong molecular ion, and ions due to consecutive loss of NO groups. However, fragmentation after loss of two NO groups was highly complex. Formation of LMO_2^+ , LMOF^+ , LMO^+ and LMF^+ (where $\text{M} = \text{Mo}, \text{W}$; $\text{L} = \beta$ -diketone ligands) appeared to be the most favourable processes. It is interesting to note that, unlike acetylacetonates of Al, Be, Cr, Mn, Zn etc. (136), no ion corresponding to LM^+ was observable in the mass spectra of $(\text{acac})_2\text{M}(\text{NO})_2$, and $(\text{tfac})_2\text{M}(\text{NO})_2$ ($\text{M} = \text{Mo}, \text{W}$), and that the ions $\text{L}_2\text{M}(\text{NO})_x^+$ ($x = 2, 1$) lost a fluorine atom instead of CF_2 , to give $\text{LM}(\text{NO})_x(\text{L-F})^+$ ($x = 2, 1$) in the mass spectra of $(\text{tfac})_2\text{M}(\text{NO})_2$ and $(\text{hfac})_2\text{M}(\text{NO})_2$. A well defined fragmentation pathway by which the ion, ML_2^+ , ($\text{M} = \text{Cr}, \text{Fe}, \text{Co}$; $\text{L} = \text{hfac}$) loses CF_2 , giving $\text{LMF}(\text{L-CF}_3)^+$ ion (137), could not be observed.

EXPERIMENTAL

All metal carbonyls $\text{M}(\text{CO})_6$ (where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and NOPF_6 were obtained from commercial sources. All solvents were used without purification. All reactions were carried out under nitrogen atmosphere. Microanalyses were performed by the microanalytical laboratory of this department and by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany. Infrared spectra were measured with a Perkin-Elmer 337 grating spectrometer and recorded in expanded form on a Hewlett-

TABLE XV

Summary of Mass Spectra of β -Diketone Compounds.^a

Fragment ^b	$(\text{acac})_2\text{M}(\text{NO})_2$		$(\text{tfac})_2\text{M}(\text{NO})_2$		$(\text{hfac})_2\text{M}(\text{NO})_2$	
	Mo	W	Mo	W	Mo	W
$\text{L}_2\text{M}(\text{NO})_2^+$	100	100	100	100	100	100
$\text{LM}(\text{NO})_2(\text{L-F})^+$	-	-	0.13	0.11	0.32	0.31
L_2MNO^+	332	154	302*	178*	157	101*
$\text{LM}(\text{NO})(\text{L-F})^+$	-	-	0.08	0.18	0.11	0.08
L_2M^+	380*	17	150	9	0.61	0.24
LMOF^+	-	-	249	74	257*	62
LMO_2^+	36	185*	-	-	-	-
LMF^+	-	-	11	2	7	7
LMO^+	64	36	-	-	-	-
LM^+	-	-	-	-	4	58

^aEntries in the table indicate abundance of fragment expressed as the abundance of the molecular ion = 100.

^b_L = β -diketone ligands. Abbreviations see Table XIV

*In assigning the base peak, m/e 43 and 69 are ignored.

Packard 7127A recorder using gaseous CO and polystyrene film for calibration purposes. NMR measurements were made on a Varian A56/60A and HA 100 instruments. Mass spectra were measured using Associated Electrical Industries MS-9 and MS-12 instruments, into which samples were introduced by direct evaporation.

Preparation of $[M(NO)_2(MeCN)_4]^{++}[PF_6]_2^-$, (M = Cr, Mo, W): To a suspension of $M(CO)_6$ in acetonitrile, $NOPF_6$ in the same solvent was added dropwise. Typically, 2.2 g. (10 mmoles) of $Cr(CO)_6$ in 50 ml. of acetonitrile was stirred vigorously at room temperature and 3.6 g. (20 mmoles) of $NOPF_6$ in 50 ml. of the same solvent was added through a dropping funnel over a period of 60 minutes. No $Cr(CO)_6$ was left at this stage, and the reaction mixture was deep brown. Concentration of the reaction mixture to about 50 ml., addition of 100 ml. of methylene chloride, followed by cooling to -80° , afforded brown crystals of product. The yield was quantitative.

Molybdenum and tungsten derivatives, $[Mo(NO)_2(MeCN)_4]^{++}[PF_6]_2^-$ and $[W(NO)_2(MeCN)_4]^{++}[PF_6]_2^-$ were prepared similarly. However, a comment is needed on the preparation of the tungsten derivative. When the reaction mixture was worked up quickly i.e., three hours after gas evolution had ceased, a different product, $[W(CO)(NO)_2(MeCN)_3]^{++}[PF_6]_2^-$ was obtained as green crystalline plates which showed a very close

resemblance to $\text{Fe}_2(\text{CO})_9$. In order to obtain $[\text{M}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$, the stirring had to be continued at least 20 hours. In the cases of preparing $[\text{Mo}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$, $[\text{W}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ and $[\text{W}(\text{CO})(\text{NO})_2(\text{MeCN})_3]^{++}[\text{PF}_6]_2^-$, the reaction mixtures showed deep-green colors. All the preparations were straightforward and quantitative.

Preparation of $[\text{W}(\text{CO})(\text{NO})_2(\text{MeCN})_3]^{++}[\text{PF}_6]_2^-$: Tungsten hexacarbonyl was reacted with NOPF_6 as described above. As soon as the gas evolution ceased, 100 ml. of methylene chloride was added to the reaction mixture and it was cooled to -80° . Fluffy green crystals came down in almost quantitative yield. These were filtered and washed with methylene chloride. Attempts to obtain corresponding chromium and molybdenum derivatives have not been successful.

Preparation of $[\text{M}(\text{NO})_2(\text{dipy})_2]^{++}[\text{PF}_6]_2^-$, (M = Cr, Mo, W): To a suspension of $[\text{M}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ in methylene chloride, 2,2'-dipyridyl was added and stirred for two days. Typically, 3.49 g. (5 mmoles) of $[\text{W}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ in 50 ml. of methylene chloride was stirred at room temperature and 1.56 g. (10 mmoles) of 2,2'-dipyridyl was added. The mixture was then stirred for two days. The starting materials disappeared and a pale-green precipitate was produced. This was filtered and washed with methylene chloride. The yield was quantitative.

Preparation of $[\text{W}(\text{NO})_2(\text{PPh}_3)_2(\text{MeCN})_2]^{++}[\text{PF}_6]_2^-$: A 2.28 g. (3 mmoles) sample of $[\text{W}(\text{CO})(\text{NO})_2(\text{MeCN})_3]^{++}[\text{PF}_6]_2^-$ was dissolved in 50 ml. of acetonitrile and 2.36 g. (9 mmoles) of triphenylphosphine was added. Immediately gas evolution was observed and the reaction mixture became red-brown. It was then heated under gentle reflux for 30 minutes. Solvent was removed under reduced pressure and extraction of the residue with methylene chloride, concentration to a small volume, followed by slow addition of n-pentane, gave pale-brown crystals of product. This was recrystallized twice from a mixture of methylene chloride and n-pentane (~10% yield). Attempts to replace all acetonitrile molecules by triphenylphosphine using excess triphenylphosphine were unsuccessful.

Preparation of $[\text{Cr}(\text{NO})_2(\text{diphos})_2]^{++}[\text{PF}_6]_2^-$: A 2.83 g. (5 mmoles) sample of $[\text{Cr}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ was suspended in 100 ml. of methylene chloride and 3.98 g. (10 mmoles) of bis(1,2-diphenylphosphinoethane) was added. It was then heated under reflux for 20 hours. The reaction mixture became deep-red. The concentration of the reaction mixture under reduced pressure, followed by slow addition of n-pentane, afforded orange crystals of product. This was recrystallized from a methylene chloride and n-pentane mixture. The yield was 80%.

Preparation of $(\text{acac})_2\text{M}(\text{NO})_2$, (M = Mo, W): A sample of $[\text{M}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ (for the preparation of $(\text{acac})_2\text{W}(\text{NO})_2$, $[\text{W}(\text{CO})(\text{NO})_2(\text{MeCN})_3]^{++}[\text{PF}_6]_2^-$ could also be employed) (5 mmoles) and thallium acetylacetonate (3.03 g., 10 mmoles) in a mixture of methylene chloride and acetonitrile (4 : 1) were heated for five hours, at refluxing temperature. The green color of $[\text{M}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ (or $[\text{W}(\text{CO})(\text{NO})_2(\text{MeCN})_3]^{++}[\text{PF}_6]_2^-$) completely disappeared to give a dark-brown solution containing a precipitate of TlPF_6 . The solvent was removed under reduced pressure, the residue was then extracted with two portions of a total of 200 ml. of n-pentane. The extract was filtered, concentrated to a small volume and cooled to -20° to afford pale-green crystals of product in an analytically pure state. Yields for $(\text{acac})_2\text{Mo}(\text{NO})_2$ and $(\text{acac})_2\text{W}(\text{NO})_2$ were 41 and 55% respectively. The corresponding chromium cation, $[\text{Cr}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$, failed to give the corresponding acetylacetonate derivative, but gave $(\text{acac})_3\text{Cr}$.

Preparation of $(\text{hfac})_2\text{M}(\text{NO})_2$, (M = Mo, W): A sample of 5 mmoles of $[\text{M}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ (or $[\text{W}(\text{CO})(\text{NO})_2(\text{MeCN})_3]^{++}[\text{PF}_6]_2^-$) and thallium hexafluoroacetylacetonate (prepared from thallium carbonate and hexafluoroacetylacetone) (4.11 g., 10 mmoles) in a mixture of methylene chloride and acetonitrile (4 : 1) were heated under gentle reflux for two hours. From the dark-brown reaction mixture,

most of the solvent was removed under reduced pressure. Since products were quite volatile, complete removal of the solvent resulted in loss of product ; thus when yellow vapour of product was observed evaporation of solvent was stopped. The residue was then extracted in three portions with 200 ml. of n-pentane. n-Pentane was removed from the extract and the product was isolated by sublimation at 20-30°/0.3 mm. onto a probe cooled by running cold water. The product $(\text{hfac})_2\text{Mo}(\text{NO})_2$ forms deep-green crystals, while $(\text{hfac})_2\text{W}(\text{NO})_2$ forms deep-brown needles.

Preparation of $(\text{tfac})_2\text{M}(\text{NO})_2$, (M = Mo, W): A sample of $[\text{M}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ (or $[\text{W}(\text{CO})(\text{NO})_2(\text{MeCN})_3]^{++}[\text{PF}_6]_2^-$) was reacted with thallous 1,1,1-trifluoroacetylacetonate (prepared by thallium carbonate and 1,1,1-trifluoroacetylacetone) as described above. The solvent was removed under reduced pressure. The green crystalline $(\text{tfac})_2\text{M}(\text{NO})_2$ was sublimed out of the residue at 90-110°/0.3 mm. onto a probe cooled with running water. Initially green oil sublimed, which eventually solidified. Yields for $(\text{tfac})_2\text{Mo}(\text{NO})_2$ and $(\text{tfac})_2\text{W}(\text{NO})_2$ were 20 and 22% respectively.

Reaction of $[\text{W}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ with Ph_4AsCl . A sample of $[\text{W}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$ (5 mmoles) was reacted with 8.36 g. (20 mmoles) of Ph_4AsCl in methanol at room temperature for 30 minutes. The reaction mixture had

a lighter color. The solvent was removed from the reaction mixture under reduced pressure. The yellow-green residue was extracted with a minimum amount of methylene chloride. Addition of n-pentane, followed by cooling to -20° , afforded light-green crystals of product. This was characterized as $[\text{Ph}_4\text{As}]^{++}[\text{W}(\text{NO})_2\text{Cl}_4]^{--}$. The latter compound was originally reported by Cotton and Johnson (121).

Reaction of $[\text{W}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^{-}$ with $\text{Co}(\text{CO})_4^{-}$:

A 3.49 g. (5 mmoles) sample of $[\text{W}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^{-}$ in 50 ml. of acetonitrile was treated with 10 mmoles of $\text{Co}(\text{CO})_4^{-}$ (prepared by dissolving $\text{Co}_2(\text{CO})_8$ in acetonitrile) at room temperature. After one hour, 100 ml. of n-pentane was added to the red reaction mixture. It was shaken for five minutes and the upper n-pentane layer contained $\text{Co}(\text{CO})_3\text{NO}$. The estimated yield was over 50%.

Effect of concentration of NOPF_6 on $\text{W}(\text{CO})_6$. To a stirred saturated solution of $\text{W}(\text{CO})_6$ in 100 ml (ca 1-2 mmoles) of acetonitrile, a diluted solution of 0.17 g. (1 mmole) of NOPF_6 in 50 ml. of the same solvent was added dropwise. The progress of the reaction was followed by infrared measurements. Addition of the first 0.5 ml. of NOPF_6 solution caused a yellow color of the reaction mixture with gas evolution, and new weak bands at ~ 2055 , ~ 2040 , ~ 2030 , ~ 1750 , ~ 1700 , and $\sim 1640 \text{ cm}^{-1}$ in the infrared

spectrum. The next addition of the same amount resulted in the disappearance of the band at 1750 cm^{-1} and new bands at 2130 and 1800 cm^{-1} became evident. During further addition of NOPF_6 , bands at 2130 , 1800 and 1700 cm^{-1} continued to increase in intensity, while the rest remained virtually the same. The former three bands were due to $[\text{W}(\text{CO})(\text{NO})_2(\text{MeCN})_3]^{++}[\text{PF}_6]_2^-$, and the latter bands were most likely to be due to some intermediate species such as $[\text{W}(\text{CO})_5\text{NO}]^+$, $[\text{W}(\text{CO})_4(\text{NO})(\text{MeCN})]^+$, $[\text{W}(\text{CO})_4(\text{NO})_2]^{++}$ or $[\text{W}(\text{CO})_2(\text{NO})_2(\text{MeCN})_2]^{++}$. Attempts to isolate the intermediate species were unsuccessful.

On the other hand, the reaction of $\text{W}(\text{CO})_6$ with four moles of NOPF_6 resulted in the isolation of only $[\text{W}(\text{CO})(\text{NO})_2(\text{MeCN})_3]^{++}[\text{PF}_6]_2^-$.

Reaction of $\text{Ph}_3\text{PW}(\text{CO})_5$ with NOPF_6 . A solution of 1.75 g. (10 mmoles) of NOPF_6 in 30 ml. of acetonitrile was added dropwise to 2.93 g. (5 mmoles) of $\text{Ph}_3\text{PW}(\text{CO})_5$ over the course of 30 minutes during which time CO was vigorously evolved. The reaction mixture was concentrated to a small volume under reduced pressure and 50 ml. of methylene chloride was added and cooled to -80° , affording 2.9 g. of green, fluffy crystals of $[\text{W}(\text{CO})(\text{NO})_2(\text{MeCN})_3]^{++}[\text{PF}_6]_2^-$. No triphenylphosphine derivative was obtained from the reaction.

Ultraviolet and visible spectra of $[M(NO)_2(MeCN)_4]^{++-}$
 $[PF_6]_2^-$ and $[W(CO)(NO)_2(MeCN)_3]^{++}[PF_6]_2^-$, (where M = Cr,

Mo, W).

UV-Visible spectra of the above four compounds are reported in Figure 19. All spectra were measured in "aged" acetonitrile solutions (refer to page 109-111).

In all cases four bands (A, B, C and D) were observed, but no attempt was made to assign these bands to possible transitions.

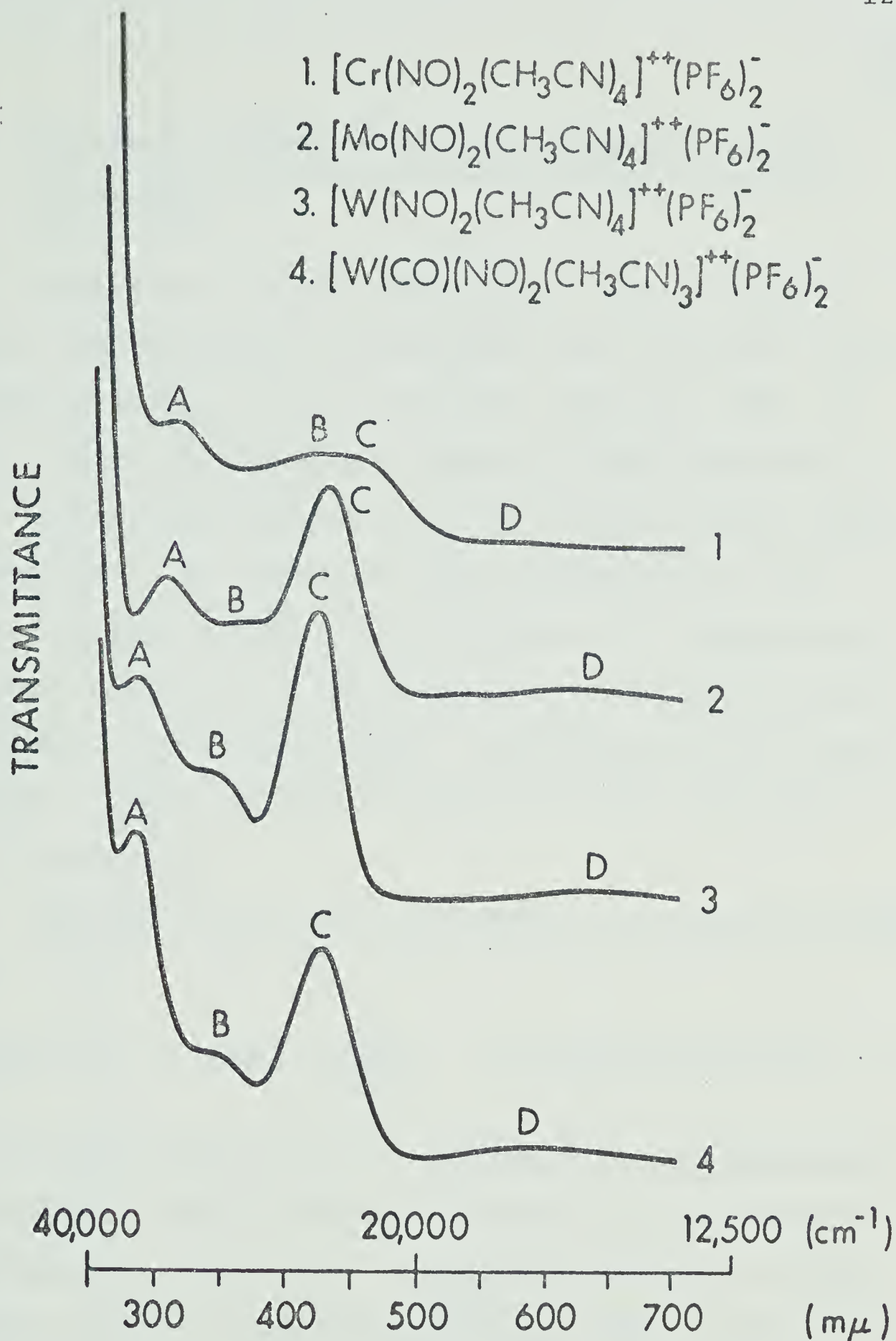
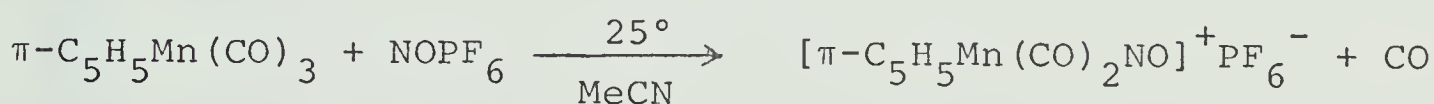


FIGURE 19 UV-Visible spectra of dinitrosyl-acetonitrile compounds of Cr, Mo, and W in acetonitrile.

B. Reactions of NOPF_6 with metal carbonyls or their derivatives.

As mentioned in the introduction, only a few successful applications of nitrosonium salts as an NO^+ source has been reported. It has now been found that NOPF_6 (or NOBF_4) reacts readily with a number of metal carbonyls or their derivatives in acetonitrile to produce several types of compounds. All reactions were carried out at room temperature by treatment of a solution (or a suspension) of metal carbonyls or their derivatives in acetonitrile with NOPF_6 in the same solvent. Reactions which are summarized in Table XVI, may be classified into three distinct categories:

(i) Reactions involving the formation of a metal-nitrosyl bond.



The reaction proceeded quite smoothly at room temperature or below with carbon monoxide evolution, and was complete in 30 minutes. Similarly, $\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_3$ gave the corresponding cation, $[\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2\text{NO}]^+\text{PF}_6^-$ (129). The method described here to prepare these cations appears to be experimentally easier and gives a higher yield of product than previous methods (116,129). The rather weak nucleophile, $\text{Co}(\text{CO})_4^-$, produced $\text{Co}(\text{CO})_3\text{NO}$ in excellent yield.

TABLE XVI

Experimental Data for the Reaction of NOPF_6 with Various Metal Carbonyls and Their

Derivatives.			
Carbonyl	Mmoles of carbonyl	Mmoles of NOPF_6	Product with approx. yield (%)
$\text{Mn}_2(\text{CO})_{10}$	10	20	$[\text{MeCNMn}(\text{CO})_5]^+ [\text{PF}_6]^-$ (95)
$\text{Re}_2(\text{CO})_{10}$	10	20	$[\text{MeCNRe}(\text{CO})_5]^+ [\text{PF}_6]^-$ (60-70)
			$[\text{Re}_2\text{O}(\text{CO})_6(\text{NO})_2(\text{MeCN})_2]^{++} [\text{PF}_6]_2^-$ (30-40)
$\text{Fe}_3(\text{CO})_{12}$	10	40-50	$\text{Fe}^{++} [\text{PF}_6]_2^-$
$\text{Fe}(\text{CO})_5$	10	10	$\text{Fe}^{++} [\text{PF}_6]_2^-$
$[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$	10	20	$[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{MeCN})]^+ [\text{PF}_6]^-$ (60)
$[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$	10	20	$[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{MeCN})_2]^+ [\text{PF}_6]^-$ (40)
$\pi\text{-C}_6\text{H}_6\text{Cr}(\text{CO})_3$	10	10	$[\text{Cr}(\text{NO})_2(\text{MeCN})_4]^{++} [\text{PF}_6]_2^-$
$\pi\text{-C}_7\text{H}_8\text{Mo}(\text{CO})_3$	10	10	$[\text{Mo}(\text{NO})_2(\text{MeCN})_4]^{++} [\text{PF}_6]_2^-$
$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$	10	10	$[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}]^+ [\text{PF}_6]^-$ (80)
$\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_3$	10	10	$[\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2\text{NO}]^+ [\text{PF}_6]^-$ (80)
$\text{Co}(\text{CO})_4^-$	10	10	$\text{Co}(\text{CO})_3\text{NO}$ (70-100)
$\text{Mn}(\text{CO})_5^-$	10	10	$\text{Mn}_2(\text{CO})_{10} : \text{Mn}(\text{CO})_4\text{NO} = 6 : 4$
$\text{Mn}(\text{CO})_5^-$	10	40	$[\text{MeCNMn}(\text{CO})_5]^+ [\text{PF}_6]^-$

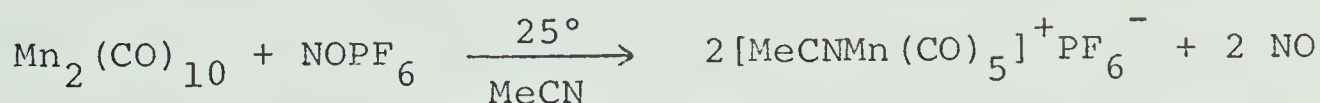
continued

Table XVI (continued)

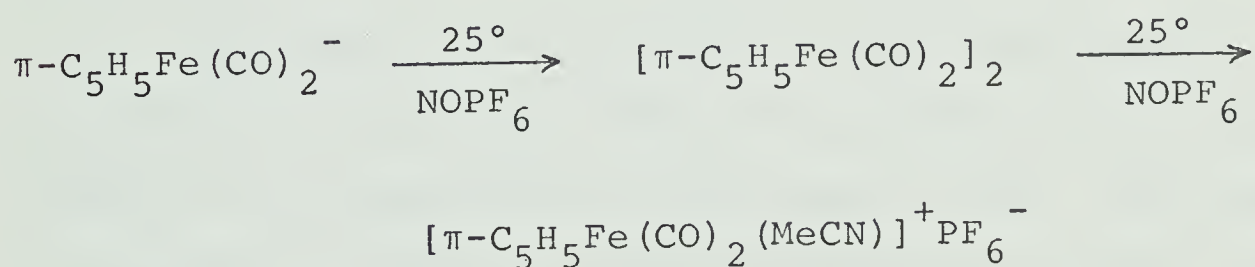
Carbonyl	Mmoles of carbonyl	Mmoles of NOPF ₆	Product with approx. yield (%)
Re (CO) ₅ ⁻	10	10	Re ₂ (CO) ₁₀
Re (CO) ₅ ⁻	10	40	[MeCNRe (CO) ₅] ⁺ [PF ₆] ⁻ (60-70)
			[Re ₂ O (CO) ₆ (NO) ₂ (MeCN) ₂] ⁺⁺ [PF ₆] ₂ ⁻ (30-40)
π-C ₅ H ₅ Mo (CO) ₃ ⁻	10	10	[π-C ₅ H ₅ Mo (CO) ₃] ₂ : π-C ₅ H ₅ Mo (CO) ₂ NO = 6 : 4
π-C ₅ H ₅ Mo (CO) ₃ ⁻	10	40	[π-C ₅ H ₅ Mo (CO) ₂ (MeCN) ₂] ⁺ [PF ₆] ⁻
			π-C ₅ H ₅ Mo (CO) ₂ NO
π-C ₅ H ₅ Fe (CO) ₂ ⁻	10	10	[π-C ₅ H ₅ Fe (CO) ₂] ₂
π-C ₅ H ₅ Fe (CO) ₂ ⁻	10	40	[π-C ₅ H ₅ Fe (CO) ₂ (MeCN)] ⁺ [PF ₆] ⁻

The latter reaction again provides an easy approach to $\text{Co}(\text{CO})_3\text{NO}$.

(ii) Reactions involving the formation of a metal-acetonitrile bond.

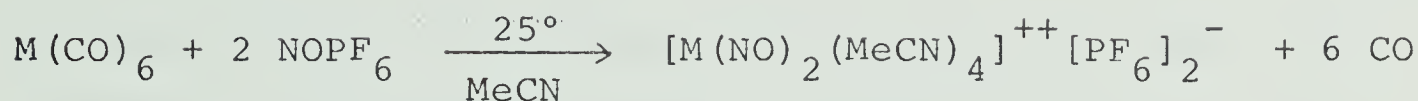


The reaction involves an oxidative cleavage of the metal-metal bond by the NO^+ . Reactions of homodimetallic carbonyl compounds such as $\text{Re}_2(\text{CO})_{10}$, $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ fall in this class. When strong nucleophiles such as $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2^-$ and $\text{Re}(\text{CO})_5^-$ were reacted with NOPF_6 , they were oxidized back to their respective dimers.



It is noteworthy that in the reaction of $\text{Re}_2(\text{CO})_{10}$ with NOPF_6 , two products were obtained. One was $[\text{MeCNRe}(\text{CO})_5]^+\text{PF}_6^-$ (60-70%), and the other was tentatively characterized as $[\text{Re}_2\text{O}(\text{CO})_6(\text{NO})_2(\text{MeCN})_2]^{++}[\text{PF}_6]_2^-$ (40-30%). The latter will be discussed later.

(iii) Reactions involving the formation of both the metal-nitrosyl and metal-acetonitrile bonds.



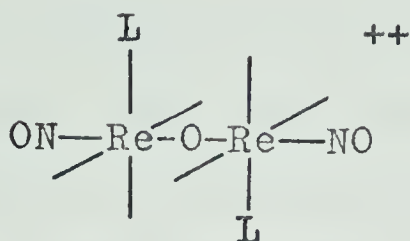
The reaction was discussed in Part A of this Chapter. Also $\pi-C_6H_6Cr(CO)_3$ and $\pi-C_7H_8Mo(CO)_3$ reacted with $NOPF_6$ to produce $[M(NO)_2(MeCN)_4]^{++} [PF_6]_2^-$ (where $M = Cr, Mo$). Thus this type of reaction appeared to be characteristic to Group VI metal carbonyls and their derivatives. Interestingly, $\pi-C_5H_5Mo(CO)_3^-$ and $Mn(CO)_5^-$, which are considered to be rather weak nucleophiles in comparison with $Re(CO)_5^-$ (or $\pi-C_5H_5Fe(CO)_2^-$), though stronger than $Co(CO)_4^-$, produced both their respective dimers and nitrosyl derivatives ($\pi-C_5H_5Mo(CO)_2NO$, $Mn(CO)_4NO$). The reactions were independent both of mole ratio of reactants and of reaction temperature.

The variation of product in the reactions of a series of carbonyl anions with $NOPF_6$ may perhaps be correlated with the nucleophilicity of the anion (138). The strong nucleophile tends to be oxidized back to its dimer, while the weak nucleophile tends to give rise to a nitrosyl derivative. Thus $\pi-C_5H_5Mo(CO)_3^-$ and $Mn(CO)_5^-$, which lie between $Re(CO)_5^-$ and $Co(CO)_4^-$, produced both their respective dimers and nitrosyl derivatives.

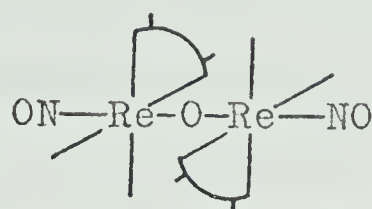
The novel rhenium compound $[Re_2O(CO)_6(NO)_2(MeCN)_2]^{++} [PF_6]_2^-$ obtained from the reaction of $Re_2(CO)_{10}$ and $NOPF_6$ formed a pale-green powder which was sparingly soluble

in acetonitrile and insoluble in methylene chloride. The infrared spectrum exhibited two carbonyl stretching bands (2131 and 2083 cm^{-1}) and one strong nitrosyl stretching band at 1820 cm^{-1} in acetonitrile, suggesting a highly symmetrical structure. The reaction between this compound and thallium acetylacetonate resulted in the isolation of a neutral compound of composition $(\text{acac})_2\text{Re}_2\text{O}(\text{CO})_4(\text{NO})_2$ which exhibited two carbonyl stretching bands at 2075 and 2008 cm^{-1} , and a nitrosyl stretching band at 1707 cm^{-1} in the infrared spectrum, while the proton NMR spectrum showed a sharp singlet at $\tau\ 7.93$ (Me groups) and a resonance at $\tau\ 4.55$ due to the methine proton in CDCl_3 . In the mass spectrum of the latter compound, the accurate mass determination of the $m/e\ 758$ which corresponds to $^{187}\text{Re}-^{185}\text{ReC}_{14}\text{H}_{14}\text{O}_{11}\text{N}_2$ gave an excellent agreement between the calculated and observed values (Calcd., 757.9677 : Found, 757.9667). Ions due to consecutive loss of four carbonyl and two nitrosyl groups from the $m/e\ 758$ ion were also unequivocally identified.

Consideration of the above spectroscopic data, together with ample precedent for a linear M-O-M bond ($[\text{Re}_2\text{OCl}_{10}]^{4-}$ (139), $[\text{Ru}_2\text{OCl}_{10}]^{4-}$ (140), $[(\text{EtOCS})_2\text{MoO}]_2\text{O}$ (141)) led us to postulate the structure XXIX and XXX for the above two rhenium compounds.



XXIX



XXX

As noted previously, reactions between nitrosylacetonitrile compounds such as $[\text{M}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$, (where $\text{M} = \text{Mo}, \text{W}$), and $[\text{Re}_2\text{O}(\text{CO})_6(\text{NO})_2(\text{MeCN})_2]^{++}[\text{PF}_6]_2^-$, and thallium β -diketonates produced β -diketone derivatives. Thus it appeared that β -diketone derivatives of rhenium tetracarbonyl might be obtainable from the reaction between $[\text{MeCNRe}(\text{CO})_5]^+\text{PF}_6^-$ and thallium β -diketonates. The latter reaction will now be discussed. From the reaction between thallium hexafluoroacetylacetonate and $[\text{MeCNRe}(\text{CO})_5]^+\text{PF}_6^-$ in methylene chloride, a hexafluoroacetylacetone derivative of rhenium carbonyl, $(\text{hfac})\text{Re}(\text{CO})_4$, could be obtained as air-stable, yellow crystals. It is readily soluble in both polar and nonpolar solvents. The infrared spectrum of the derivative exhibited four carbonyl stretching bands at 2123(w), 2026(s), 2012(s) and 1968(s) cm^{-1} in cyclohexane. The number of bands and their relative intensities are in accord with the pattern predicted for a complex of the type cis- $\text{M}(\text{CO})_4\text{X}_2$ (point group C_{2v}). The ^{19}F spectrum

showed a singlet at 76.0 ϕ upfield from the internal CFCl_3 reference. The mass spectrum possessed LRe(CO)_x^+ (where $\text{L} = \text{hfac}$; $x = 4, 3, 2, 1, 0$) as well as $\text{Re(CO)}_x(\text{L-F})^+$ (where $x = 4, 3$), $\text{Re(CO)}_x(\text{L-2F})^+$ (where $x = 3, 2$) and $\text{ReF(L-CF}_3)^+$.

The attempted preparation of $(\text{acac})\text{Re(CO)}_4$ from thallium acetylacetonate and $[\text{MeCNRe(CO)}_5]^+\text{PF}_6^-$ yielded an unstable yellow-orange solid. The infrared spectrum of this solid exhibited four bands in the carbonyl stretching region at 2099(s), 2041(w), 2022(s) and 1897(s) cm^{-1} in methylene chloride. The mass spectrum of the solid exhibited the molecular ion as well as ions due to consecutive loss of four carbonyl groups from the molecular ion. However, the proton spectrum consisted of three methyl resonances around τ 8.0 with unequal intensities; one strong and two weak. The above data suggested that the solid was the anticipated product which might be a mixture of monomer and polymer. However, instability of the compound precluded consistent analytical data. This is somewhat similar to the unsuccessful attempt to isolate the corresponding manganese derivative (142).

EXPERIMENTAL

Reagents and general procedures are the same as described in Part A. Compounds discussed here are listed in Table XVII.

TABLE XVII

Analytical Data, Melting Points and Colors of Some Miscellaneous Compounds

Compound	M.p. (°C)	Color	Calcd%		Found%		
			C	H	N	C	H N
$[\text{MeCNMn}(\text{CO})_5]^{+}[\text{PF}_6]^{-}$	dec 145	White	22.07	0.79	3.58	22.25	0.80 3.67
$[\text{MeCNRe}(\text{CO})_5]^{+}[\text{PF}_6]^{-}$	dec 155	White	16.41	0.59	2.73	16.50	0.71 2.78
$[\text{Re}_2\text{O}(\text{CO})_6(\text{NO})_2(\text{MeCN})_2]^{++}[\text{PF}_6]_2^{-}$ dec	160	Pale green	12.15	0.61	5.67	12.56	0.88 5.69
$\text{Re}_2\text{O}(\text{CO})_4(\text{NO})_2(\text{acac})_2$	176-177	Yellow	22.16	1.86	3.69	22.35	2.07 3.64
$[(\text{OC})_4\text{Re}(\text{PPh}_3)_2]^{+}\text{PF}_6^{-}$ a	dec 150	White	49.64	3.12	-	49.87	3.59 -
$(\text{hfac})\text{Re}(\text{CO})_4$	82	Yellow	21.39	0.20	-	21.31	0.84 -

a Known cation (see text).

Preparation of $[\text{MeCNMn}(\text{CO})_5]^+\text{PF}_6^-$: To a suspension of 3.90 g. (10 mmoles) $\text{Mn}_2(\text{CO})_{10}$ in 50 ml. of acetonitrile, 3.50 g. (20 mmoles) NOPF_6 in the same solvent was added through a dropping funnel over the course of 60 minutes during which time NO was evolved. From the clear yellow reaction mixture, the solvent was removed under reduced pressure, resulting in a cream-colored crystalline material. This crude product was washed with several aliquots of methylene chloride, yielding 7.2 g. of $[\text{MeCNMn}(\text{CO})_5]^+\text{PF}_6^-$ (93% yield based on $\text{Mn}_2(\text{CO})_{10}$ employed). The infrared spectrum of this compound exhibited carbonyl stretching bands at 2163(w), 2116(w), 2080(vs) and 2043(m) cm^{-1} in methylene chloride. The proton NMR spectrum exhibited a sharp singlet at τ 7.70 due to the coordinated acetonitrile group and the ^{19}F spectrum possessed two resonance lines at 74.5 and 86.5 ϕ from CFCl_3 external reference with $J_{\text{PF}} = 675$ cps, in CD_3CN .

Similarly, $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ reacted with NOPF_6 to produce the known cations, $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{MeCN})]^+\text{PF}_6^-$ (143) and $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{MeCN})_2]^+\text{PF}_6^-$ (144) respectively.

Preparation of $[\text{MeCNRe}(\text{CO})_5]^+\text{PF}_6^-$ and $[\text{Re}_2\text{O}(\text{CO})_6(\text{NO})_2\text{-(MeCN)}_2]^{++}[\text{PF}_6]_2^-$: To a suspension of 6.52 g. (10 mmoles) of $\text{Re}_2(\text{CO})_{10}$ in 50 ml. of acetonitrile, 3.50 g. (20 mmoles) of NOPF_6 in 20 ml. of the same solvent was added dropwise

at room temperature. Gas evolution was observed and a different precipitate came down. This precipitate was filtered and washed with several aliquots of methylene chloride, affording 4.2 g. of a very pale-green powder of $[\text{Re}_2\text{O}(\text{CO})_6(\text{NO})_2(\text{MeCN})_2]^{++}[\text{PF}_6]_2^-$ (42% yield). Diamagnetism of this compound would account for the single sharp resonance at τ 7.44 due to the coordinated acetonitrile group in CD_3CN .

The filtrate from the straight reaction mixture was concentrated and an equal volume of methylene chloride was added. This was cooled to -20° to afford pale-brown crystals of $[\text{MeCNRe}(\text{CO})_5]^+\text{PF}_6^-$. Recrystallization from a mixture of acetonitrile and methylene chloride gave white crystals of product in an analytically pure state. Yields ranged from 60 to 70%.

Preparation of $(\text{acac})_2\text{Re}_2\text{O}(\text{CO})_4(\text{NO})_2$: A suspension of $[\text{Re}_2\text{O}(\text{CO})_6(\text{NO})_2(\text{MeCN})_2]^{++}[\text{PF}_6]_2^-$ (4.0 g., 4.05 mmoles) and thallium acetylacetonate (2.46 g., 8.1 mmoles) in 100 ml. of methylene chloride was heated at gentle refluxing temperature for 15 hours. The solvent was removed under reduced pressure and the residue was extracted with several portions of a total of 300 ml. of n-pentane. It was concentrated to about 50 ml. and cooled to -20° to afford 0.3 g. of yellow plates of product. This was recrystallized from n-pentane (9% yield).

Preparation of $(\text{hfac})\text{Re}(\text{CO})_4$: A suspension of thallium hexafluoroacetylacetonate (2.05 g., 5 mmoles) and $[\text{MeCNRe}(\text{CO})_5]^+\text{PF}_6^-$ (2.56 g., 5 mmoles) in 100 ml. of methylene chloride was heated at refluxing temperature for 15 hours. From the brown reaction mixture the solvent was removed under reduced pressure. Product sublimed from the residue at $50-60^\circ/0.3$ mm. onto a probe cooled with running water to give 0.9 g. of yellow crystals. This contained $\text{Re}_2(\text{CO})_{10}$, and $(\text{hfac})\text{Re}(\text{CO})_4$ was separated from the latter by fractional sublimation (a final yield 0.4 g., 20%).

Similarly, thallium acetylacetonate was reacted with $[\text{MeCNRe}(\text{CO})_5]^+\text{PF}_6^-$. The reaction mixture was evaporated and the residue was sublimed at $110^\circ/0.3$ mm. onto a probe cooled with running water to afford 0.75 g. of a yellow-orange solid.

Reaction of NOPF_6 with various carbonyl anions: The acetonitrile solution of carbonyl anion was prepared by the reduction of carbonyl dimer with excess 1% sodium amalgam in dry THF, followed by removal of the THF under high vacuum and dissolving the residue (sodium salt of carbonyl anion) in acetonitrile. The acetonitrile solution thus prepared was then treated with NOPF_6 as described above. Neutral products were usually isolated by extraction of the reaction mixture with n-pentane, while ionic products were obtained by reduction of their solubilities

in acetonitrile with addition of methylene chloride and n-pentane.

Typically, 1.95 g. (5 mmoles) of $\text{Mn}_2(\text{CO})_{10}$ in 100 ml. of dry THF was stirred vigorously with excess of 1% sodium amalgam for 90 minutes at room temperature. The THF solution containing 10 mmoles of $\text{NaMn}(\text{CO})_5$ was transferred to a 300 ml. round bottom flask and the THF was removed under high vacuum ($25^\circ/0.1$ mm.), leaving a white to pale green powder. This was dissolved in 50 ml. of acetonitrile. To this acetonitrile solution of $\text{NaMn}(\text{CO})_5$, 10 or 40 mmoles of NOPF_6 in the same solvent was added dropwise over the course of 10-30 minutes during which period CO gas evolved. The red-brown reaction mixture was then extracted with 200 ml. of n-pentane. The extract contained $\text{Mn}_2(\text{CO})_{10}$ and $\text{Mn}(\text{CO})_4\text{NO}$ (the latter exhibited $\nu(\text{CO})$ at 2096(w), 2026(s), 1981(s), and $\nu(\text{NO})$ at 1768 cm^{-1} in n-pentane, these may be compared with those reported; 2095(w), 2019(s), 1972(s) and 1759 cm^{-1} in tetrachloroethylene (115)), with approximate mole ratio of 6 : 4 based on band intensities. The product distribution in the reaction carried out at -65° was found to be virtually the same as above.

Reaction of NOPF_6 with $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3$ (M = Mn, Re):

A solution of NOPF_6 (1.75 g., 10 mmoles) in 20 ml of acetonitrile was added dropwise to 10 mmoles of

$\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3$ (M = Mn, Re) in 50 ml. of the same solvent over a period of 10 minutes during which time CO was evolved. After concentration of the reaction mixture to a small volume, addition of methylene chloride and n-pentane afforded a yellow precipitate of product, which was recrystallized from a mixture of acetonitrile, methylene chloride and n-pentane affording an 80% yield of product. The reaction could also be done by addition of an acetonitrile solution of the carbonyls to NOPF_6 in the same solvent.

Reaction of PPh_3 with $[\text{MeCNRe}(\text{CO})_5]^+\text{PF}_6^-$: A solution of triphenylphosphine (2.62 g., 10 mmoles) and $[\text{MeCNRe}(\text{CO})_5]^+\text{PF}_6^-$ (2.56 g., 5 mmoles) in 100 ml. of an acetone-methanol mixture (1 : 1 by volume) was heated at refluxing temperature for 15 hours. The brown reaction mixture was allowed to cool to room temperature, affording a massive precipitate of product. This was recrystallized from hot methanol to give an 80% yield of product, and this was characterized as a mixture of cis and trans isomers of $[(\text{CO})_4\text{Re}(\text{PPh}_3)_2]^+\text{PF}_6^-$. The reaction was not stereospecific, product exhibiting carbonyl stretching bands at 2079(w), 2050(s), 2037(w), 1970(s) and 1949(s) cm^{-1} in acetonitrile consistent with a mixture of cis ($2\text{A}_1 + \text{B}_1 + \text{B}_2$) and trans (E_u) isomers. The latter trans isomer was reported by Kruck and Höfler (145).

Reaction of NOPF_6 with $\text{Fe}(\text{CO})_5$: A solution of

$\text{Fe}(\text{CO})_5$ (1.96 g., 10 mmoles) in 50 ml. of acetonitrile was treated with NOPF_6 (1.75 g., 10 mmoles) in 20 ml. of the same solvent. After gas evolution had ceased, volatiles were removed under reduced pressure leaving colorless crystals. These were extremely moisture sensitive and turned out to be $\text{Fe}^{++}[\text{PF}_6]_2^-$. Similarly, $\text{Fe}_3(\text{CO})_{12}$ gave the identical product.

Reaction of NOPF_6 with $\pi\text{-C}_6\text{H}_6\text{Cr}(\text{CO})_3$: To a stirred suspension of $\pi\text{-C}_6\text{H}_6\text{Cr}(\text{CO})_3$ (1.86 g., 10 mmoles) in 50 ml. of acetonitrile, NOPF_6 (1.75 g., 10 mmoles) in 20 ml. of the same solvent was added dropwise, to produce the $[\text{Cr}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]_2^-$. Similarly, $\pi\text{-C}_7\text{H}_8\text{Mo}(\text{CO})_3$ produced the corresponding molybdenum derivative, $[\text{Mo}(\text{NO})_2(\text{MeCN})_4]^{++}[\text{PF}_6]$. These compounds have already been discussed in Part A.

CHAPTER VSome Miscellaneous Compounds

In this Chapter, five independent investigations of some transition metal compounds are discussed:

1. Some reactions of $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$.
2. Some reactions of $[\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2\text{NO}]^+[\text{PF}_6]^-$.
3. Preparation and properties of $\text{Cl}_3\text{SiFe}(\text{CO})_3\text{NO}$.
4. Preparation and properties of $\text{Co}_3(\text{CO})_{10}\text{BHNMe}_2\text{BH}_2\text{NMe}_2$.
5. Preparation and properties of dimethylphenylphosphine derivatives of 1,2,3-triphenylcyclopropenylcobalt-carbonyl.

New compounds discussed in this Chapter are listed in Table XVIII together with analytical data, melting points and colors. The first three refer to Chapter IV and the last investigation refers to Chapter I.

TABLE XVIII

Analytical Data, Melting Points and Colors of Some Miscellaneous Compounds

Compound	Color	M.p. (°C)	Calcd%			Found%		
			C	H	N	C	H	N
$\text{CF}_3\text{CO}_2\text{Cr}(\text{NO})_2(\pi\text{-C}_5\text{H}_5)$	Green	92	28.98	1.86	9.66	28.91	1.67	9.72
$\text{Cl}_3\text{SnCr}(\text{NO})_2(\pi\text{-C}_5\text{H}_5)^{\text{a}}$	Green	134	14.93	1.25	6.97	15.16	1.08	6.97
$\text{Br}_3\text{SnCr}(\text{NO})_2(\pi\text{-C}_5\text{H}_5)^{\text{b}}$	Green	104	11.21	0.94	5.23	11.15	1.11	5.27
$\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})(\text{NO})\text{CH}_3^{\text{c}}$	Red	75	25.92	2.49	4.32	25.58	2.45	4.68
$\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})(\text{NO})\text{I}^{\text{d}}$	Black	147	16.52	1.16	3.21	15.86	1.21	3.35
$[\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})(\text{NO})]_2^{\text{e}}$	Black	dec 250	23.30	1.63	4.53	25.23	2.44	-
$\text{Cl}_3\text{SiFe}(\text{CO})_3\text{NO}^{\text{f}}$	Orange	56	11.85	-	4.60	11.80	-	4.61
$\text{Co}_3(\text{CO})_{10}\text{BHNMe}_2\text{BH}_2\text{NMe}_2$	Violet	78	29.52	2.65	4.92	28.90	2.84	5.17
$\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_3\text{PMe}_2\text{Ph}$	Orange	152	70.08	4.78	-	69.94	5.01	-
$\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})_2$	Orange	163	71.13	5.66	-	71.01	5.59	-

^a Chlorine: Calculated, 26.45; Found, 26.53

^b Bromine: Calculated, 44.77; Found, 45.31.

^c Oxygen: Calculated, 9.87; Found, 9.71

^d Iodine: Calculated, 29.09; Found, 28.64.

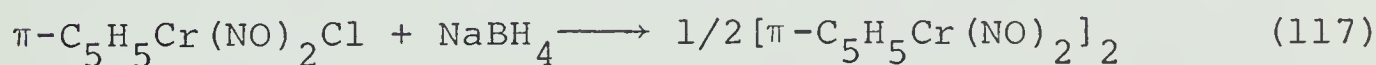
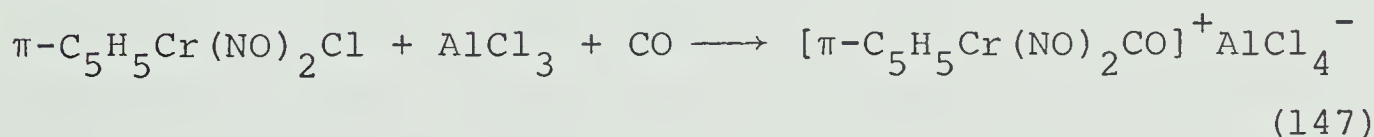
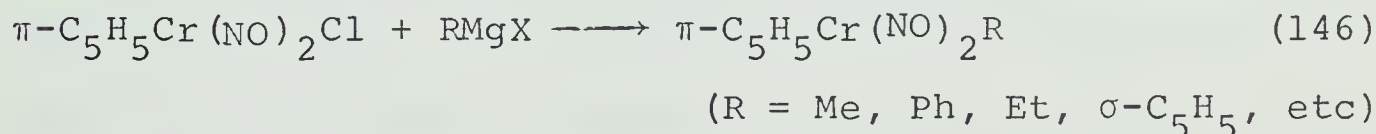
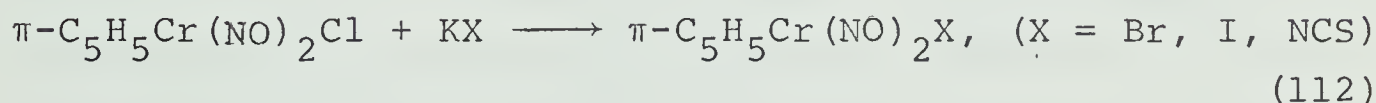
^e Not enough sample was available for the complete analysis

^f Chlorine: Calculated, 34.95; Found, 34.66

1. Some reactions of $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$

INTRODUCTION

In 1956, π -cyclopentadienyldinitrosylchromium chloride was reported (112). Subsequently, this compound has been a useful intermediate for the synthesis of other π -cyclopentadienyldinitrosylchromium derivatives. These are of the following types:



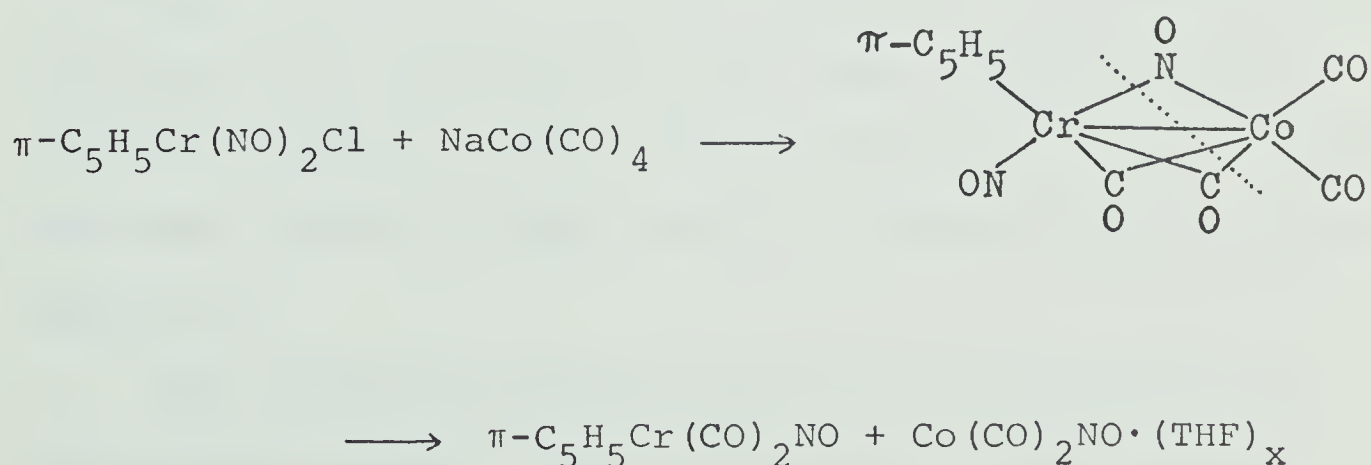
The cationic species, $[\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{CO}]^+$, was isolated as the hexafluorophosphate salt, $[\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{CO}]^+\text{PF}_6^-$, which reacts with triphenylphosphine to produce $[\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{PPh}_3]^+\text{PF}_6^-$ (101).

The reactions investigated in the present work were (i) halide displacement reactions by transition metal carbonyl anions, (ii) insertion reactions of SnX_2 (X = Cl, Br) into the Cr-X bond.

RESULTS AND DISCUSSION

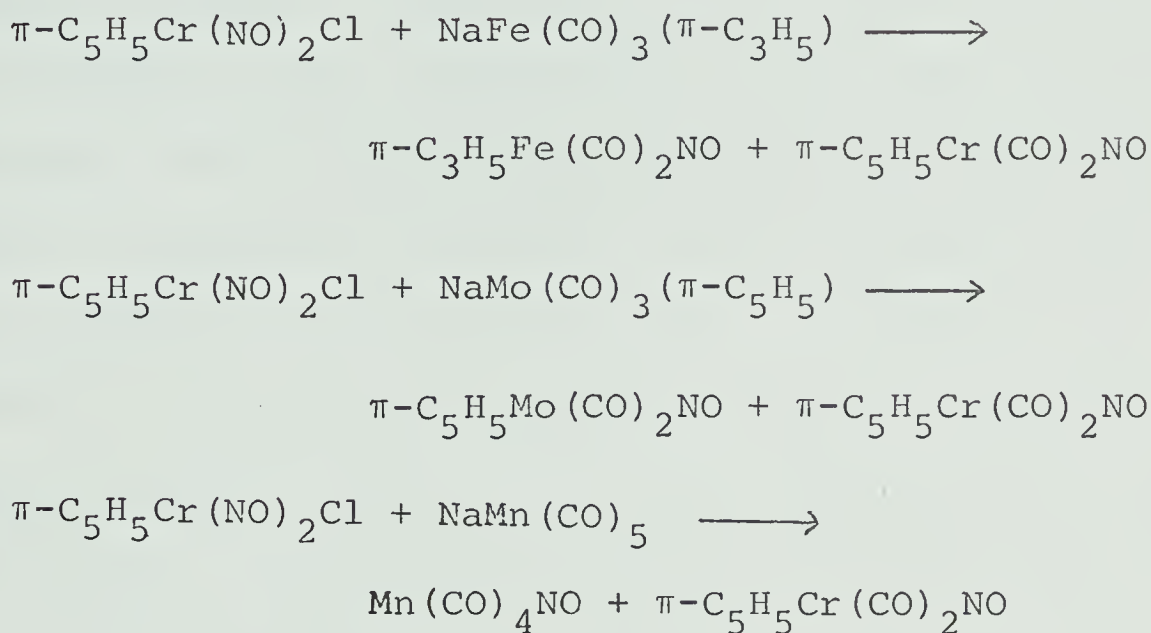
Attempts to reduce $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$ with sodium amalgam to the anion, $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2^-$, resulted in decomposition of the starting material. Apparently reaction occurred, but no evidence for the presence of the anion could be obtained from the reaction mixture.

Several transition metal carbonyl anions were reacted with $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$. The reaction between $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$ and $\text{NaCo}(\text{CO})_4$ in THF gave the known $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{NO}$ in 75% yield based on the chloride employed. The most striking feature of this reaction was that the two transition metals exchanged ligands with each other, which is surprising considering the relative inertness of nitrosyl groups to substitution. This in turn suggested that the Cr-Co bond had initially formed, and that the intermediate " $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{-Co}(\text{CO})_4$ " which could have the bridged structure as shown in the following equation, could not survive under the experimental conditions:



The $\text{Co}(\text{CO})_2\text{NO} \cdot (\text{THF})_x$ may well decompose.

There is some evidence in support of the above reaction scheme as the following reactions show:



It is interesting to note at this stage that treatment of $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$ with $\text{NaRe}(\text{CO})_5$ gave only $\text{Re}_2(\text{CO})_{10}$, which would perhaps be a result of rhenium not forming bridges.

The reaction of $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$ with $\text{NaCo}(\text{CO})_4$ provides an easier route to prepare $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{NO}$ than the existing method (112). Attempts to obtain the latter nitrosyl derivative in higher yields by treatment of the chloride with $\text{NaCr}(\text{CO})_3(\pi\text{-C}_5\text{H}_5)$ under carbon monoxide pressure (about 60 psi.) were not fruitful, giving almost the same yields as those obtained from the reaction with $\text{NaCo}(\text{CO})_4$.

The reaction between silver trifluoroacetate and the halide yielded $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{OCOCF}_3$. This reaction

parallels the formation of carbonyl analogues from metal carbonyl halides (148).

Finally, $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$ was reacted with SnCl_2 in benzene to produce $\text{Cl}_3\text{SnCr}(\text{NO})_2(\pi\text{-C}_5\text{H}_5)$. The compound is an air-stable, green, crystalline solid. The infrared spectrum of the new compound in the nitrosyl stretching region (in methylene chloride solution) exhibited two strong bands at 1827 and 1738 cm^{-1} . Similarly, $\text{Br}_3\text{-SnCr}(\text{NO})_2(\pi\text{-C}_5\text{H}_5)$ could be obtained as green crystals. The infrared spectrum showed two NO stretching bands at 1823 and 1735 cm^{-1} in methylene chloride. In both cases the lower frequency band was more intense than the higher frequency one. This method again parallels the formation of the carbonyl analogues (57).

EXPERIMENTAL

A common procedure employed the reduction of a dimeric or trimeric metal carbonyl derivative [$\text{Co}_2(\text{CO})_8$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$, $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$, $\text{Fe}_3(\text{CO})_{12}$] or a metal carbonyl halide ($\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Br}$) with excess of 1% sodium amalgam in dry THF solution. Reaction of the resulting anionic species with $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$ (prepared by the method described by King (127)) was carried out by the addition of the latter chloride in the same solvent at room temperature.

Typically, 1.71 g. (5 mmoles) of dicobalt octacarbonyl in 100 ml. of freshly dried THF and excess of 1% sodium amalgam were stirred vigorously for 60 minutes, and the excess amalgam was drained off. To the THF solution of NaCo(CO)_4 , 2.12 g. (10 mmoles) of $\pi\text{-C}_5\text{H}_5\text{Cr(NO)}_2\text{Cl}$ in 20 ml. of the same solvent was added. After being stirred for 30 minutes, solvent was removed on a rotary evaporator using a water-aspirator. The residue was extracted with 200 ml. of n-pentane. The extract was concentrated and cooled to -80° to yield 1.55 g. (76%) of product, which was recrystallized from a methylene chloride-pentane mixture. When volatile products ($\pi\text{-C}_3\text{H}_5\text{Fe(CO)}_2\text{NO}$ and $\text{Mn(CO)}_4\text{NO}$) were produced, products were purified by sublimation.

Unfortunately, all reactions between $\pi\text{-C}_5\text{H}_5\text{Cr(NO)}_2\text{Cl}$ and LiMPh_3 (where $\text{M} = \text{Si, Ge, Sn}$) were unsuccessful.

Preparation of $\text{Cl}_3\text{SnCr(NO)}_2(\pi\text{-C}_5\text{H}_5)$: A suspension of $\pi\text{-C}_5\text{H}_5\text{Cr(NO)}_2\text{Cl}$ (2.12 g., 10 mmoles) and stannous chloride (1.89 g., 10 mmoles) in 100 ml. of benzene was heated at refluxing temperature for 24 hours. The solvent was removed under reduced pressure. The residue was extracted with 50 ml. of methylene chloride and the extract was filtered and concentrated to a small volume. Addition of 50 ml. of n-pentane to the green solution produced immediately green crystalline plates of product. An additional recrystallization afforded an analytical sample (1.81 g.,

45% yield). Similarly, $\text{Br}_3\text{SnCr}(\text{NO})_2(\pi\text{-C}_5\text{H}_5)$ was prepared using $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Br}$ and stannous bromide (3.87 g., 72% yield).

Preparation of $\text{CF}_3\text{CO}_2\text{Cr}(\text{NO})_2(\pi\text{-C}_5\text{H}_5)$: To a stirred solution of $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$ in methylene chloride, an equimolar amount of silver trifluoroacetate was added. The reaction was complete in one minute as silver chloride precipitated from the solution. The reaction mixture was filtered and concentrated to a few ml. to afford green crystals of product, which was recrystallized from a mixture of methylene chloride and n-pentane (90% yield). The infrared spectrum showed two NO stretching bands at 1829 and 1720 cm^{-1} , and a ketonic band at 1700 cm^{-1} as a shoulder. The proton NMR spectrum exhibited a sharp singlet at τ 4.26, while the ^{19}F resonance at 74.6 ϕ from internal CFCl_3 in methylene chloride. The mass spectrum possessed fragments corresponding to consecutive loss of two NO groups from the molecular ion, and also the fragments $\text{C}_5\text{H}_5\text{Cr}(\text{NO})_x^+$ (where $x = 2, 1, 0$) involving loss of the trifluoroacetate group.

2. Some reactions of $[\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2\text{NO}]^+\text{PF}_6^-$

INTRODUCTION

As mentioned in Chapter IV, a few reactions of $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}]^+\text{PF}_6^-$ are known and more recently James and McCleverty have reported several interesting reactions between the cation and a number of ligands (149). This work was initiated to obtain new compounds which were derivable from the cation $[\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2\text{NO}]^+$.

RESULTS AND DISCUSSION

The reaction between $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}]^+\text{PF}_6^-$ and NaBH_4 has been shown to produce $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})(\text{NO})]_2$ (117). In contrast to this observation, it has now been found that the reaction of the corresponding rhenium cation with NaBH_4 in THF results in the formation of $\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})(\text{NO})\text{Me}$, and no dimer was formed in this reaction. The relatively high yield (ca. 50%) of the methyl derivative suggested a continuous reduction of one of the carbonyl groups by BH_4^- ion, and precluded the only other plausible route by which the methyl group could arise, that is, from the solvent. A similar phenomenon has been observed in the reaction of $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{L}]^+$ (where $\text{M} = \text{Mo}, \text{W}$; $\text{L} = \text{PPh}_3$) with BH_4^- (150).

The methyl derivative $\pi\text{-C}_5\text{H}_5\text{Re(CO)(NO)Me}$ was stable in air for long periods, while the solution was slowly oxidized over a period of 20 hours. The infrared spectrum was consistent with a carbonylnitrosyl compound (a strong $\nu(\text{CO})$ at 1792 cm^{-1} and $\nu(\text{NO})$ at 1715 cm^{-1} in cyclohexane). The proton NMR spectrum in CDCl_3 consisted of two sharp singlets one (τ 4.42) arising from the π -cyclopentadienyl ring protons and the other (τ 9.05) typical of a methyl group, with intensity ratio of 5 : 3. In the mass spectrum the parent ion was the base peak, and ions due to loss of a methyl, CO or NO group from the parent ion were unambiguously identified. However, ions which were found in the range from m/e 282 ($\pi\text{-C}_5\text{H}_5\text{ReNO}^+$) to m/e 187 (Re^+) were somewhat more complex. These were tentatively $\pi\text{-C}_5\text{H}_5\text{ReHCH}_3^+$ (s), $\pi\text{-C}_5\text{H}_5\text{ReCH}_2^+$ (s), $\pi\text{-C}_5\text{H}_5\text{ReCH}^+$ (s), $\pi\text{-C}_5\text{H}_5\text{ReH}_3^+$ (m), $\pi\text{-C}_5\text{H}_5\text{ReH}^+$ (m), ReC_3H^+ (m), ReC_2H_2^+ (m), ReC_2H^+ (m), ReCH^+ (m) and ReC^+ (w). Furthermore, a weak ion of m/e 336 (P^++11) suggested a possibility that some borane adduct such as $\pi\text{-C}_5\text{H}_5\text{Re(CO)(NO)Me:BH}_3$ was present in the sample, although the result of boron analysis was 0.00%. The divalent ions such as P^{++} , $\pi\text{-C}_5\text{H}_5\text{Re(CO)Me}^{++}$, $\pi\text{-C}_5\text{H}_5\text{ReNO}^{++}$, $\pi\text{-C}_5\text{H}_5\text{ReCH}_2^{++}$ and $\pi\text{-C}_5\text{H}_5\text{ReH}^{++}$ were observed in moderate to high abundances.

The methyl derivative reacted with iodine in acetone to produce $\pi\text{-C}_5\text{H}_5\text{Re(CO)(NO)I}$, which exhibited a

carbonyl stretching band at 1999 cm^{-1} and a nitrosyl stretching band at 1737 cm^{-1} respectively in methylene chloride, and the proton NMR spectrum showed a singlet at $\tau\ 7.13$ in CDCl_3 . The reaction parallels the formation of $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{X}$ (where $\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) from their alkyl or aryl derivatives (146).

The manganese cation $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{NO}]^+$ has been shown to react with triethylamine to produce $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})(\text{NO})]_2$ (149). Thus the corresponding rhenium dimer appeared to be obtainable in a similar manner, and from the reaction of the $[\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2\text{NO}]^+$ ion with triethylamine, black crystals in exceedingly small amount could be obtained. Unfortunately, the yield was too low to permit isolation of any of the compound in later attempts to repeat this preparation, although infrared spectroscopy indicated that some was formed. The characterization of these black crystals by mass, NMR and infrared spectra suggested that they were the desired $[\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})(\text{NO})]_2$. The mass spectrum exhibited the strong molecular ion, and ions of $(\pi\text{-C}_5\text{H}_5)_2\text{Re}_2(\text{CO})(\text{NO})_2^+$, $(\pi\text{-C}_5\text{H}_5)_2\text{Re}_2(\text{NO})_2^+$, $(\pi\text{-C}_5\text{H}_5)_2\text{Re}_2^-(\text{CO})(\text{NO})^+$, $(\pi\text{-C}_5\text{H}_5)_2\text{Re}_2(\text{NO})^+$, $(\pi\text{-C}_5\text{H}_5)_2\text{Re}_2\text{H}_3^+$ and $(\pi\text{-C}_5\text{H}_5)_2\text{Re}_2\text{H}^+$, while the ion which had lost all carbonyl and nitrosyl groups from the parent ion was not observed. The proton NMR spectrum showed two sharp singlets with an intensity ratio of 1 : 1 at $\tau\ 4.29$ and $\tau\ 4.40$ in CDCl_3 .

solution, which indicated the diamagnetism of this compound. The infrared spectrum in the carbonyl and nitrosyl stretching regions exhibited five bands at 1955(s), 1930(s), 1728(m), 1680(s,sh) and 1670(s) cm^{-1} in methylene chloride solution. Thus the dimer appeared to exist as a mixture of two configurations, presumably the cis and trans forms.

EXPERIMENTAL

Reagents and general procedure are the same as described in Chapter IV. The cation, $[\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2\text{NO}]^+$ was prepared by the method described in Part B, Chapter IV.

Preparation of $\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})(\text{NO})\text{Me}$: To a suspension of $[\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2\text{NO}]^+\text{PF}_6^-$ (3.7 g., 7.7 mmoles) in dry THF (50 ml.) was added, with magnetic stirring, sodium borohydride (2.0 g., 53 mmoles). It was then stirred at room temperature for 30 minutes. The reaction mixture had a dark red-brown color. The THF was removed under reduced pressure and the residue was sublimed at $50^\circ/0.3$ mm. onto a probe cooled by running water to give a red sublimate of product. M.p. 75° , 1.3 g., 52% yield based on the cation used.

Preparation of $\pi\text{-C}_5\text{H}_5\text{Re(CO)(NO)I}$: A 0.33 g. (1 mmole) sample of $\pi\text{-C}_5\text{H}_5\text{Re(CO)(NO)Me}$ in 20 ml. of chloroform was treated with iodine (0.45 g., 1 mmole) at room temperature. The solution was stirred for 60 minutes. The solvent was removed under reduced pressure and unreacted starting materials were sublimed off from the residue. The black solid from the above operation was dissolved in a minimum amount of methylene chloride and n-pentane was added to give black crystals of product (0.20 g., 46% yield).

Preparation of $[\pi\text{-C}_5\text{H}_5\text{Re(CO)(NO)}]_2$: The cation $[\pi\text{-C}_5\text{H}_5\text{Re(CO)}_2\text{NO}]^+\text{PF}_6^-$ (3.0 g., 6.2 mmoles) dissolved in 50 ml. of acetone was treated with 2.0 ml. of triethylamine. Immediate color change from a yellow-orange to a dark red-brown was observed. The mixture was then heated at a gentle refluxing temperature for 30 minutes. Volatiles were removed under reduced pressure from the reaction mixture and the residue was chromatographed (Al_2O_3 , acetone as eluant). The first pale-brown band gave a deep-red solution which was evaporated and the residue was dissolved in a minimum amount of methylene chloride and n-pentane was added. It was cooled to -20° to give 50 mg. of black crystals of product (0.8% yield). The compound was soluble in acetone, methylene chloride and chloroform to give red-brown, air-stable solutions. Unlike the corresponding manganese dimer, the rhenium dimer was air-stable and only slowly decomposed at 250° .

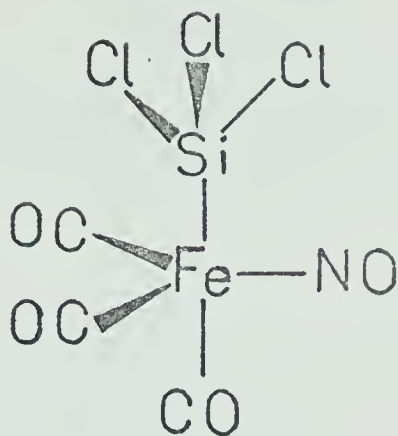
3. Preparation and properties of $\text{Cl}_3\text{SiFe}(\text{CO})_3\text{NO}$

INTRODUCTION

Some time ago, Piper and Wilkinson prepared $\pi\text{-C}_5\text{H}_5\text{-Mo}(\text{CO})_2\text{NO}$ by the reaction of $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$ and N-nitroso-N-methyl-p-toluenesulfonamide (146), later Treichel, Pitcher, King and Stone obtained $\text{Mn}(\text{CO})_4\text{NO}$ by treatment of $\text{HMn}(\text{CO})_5$ with the reagent which is commercially available under the name "Diazald" (115). It appeared that "Diazald" might be reactive towards $\text{Cl}_3\text{SiFe}(\text{CO})_4\text{H}$ or $\text{Ph}_3\text{SiFe}(\text{CO})_4\text{H}$. Effort directed to investigate this possibility was described.

RESULTS AND DISCUSSION

Hydridotrichlorosilyltetracarbonyliron (151), $\text{Cl}_3\text{SiFe}(\text{CO})_4\text{H}$, was found to react with Diazald in diethyl-ether to give $\text{Cl}_3\text{SiFe}(\text{CO})_3\text{NO}$, which was isolated in 40% yield as moderately air-stable orange crystals. The infrared spectrum of the compound exhibited three terminal carbonyl stretching bands at 2098(s), 2052(s) and 2021(s) cm^{-1} , and one strong terminal nitrosyl stretching band at 1818 cm^{-1} . The most obvious implication of the infrared spectrum was that the molecular configuration had C_s point symmetry and that the nitrosyl group occupied one of the equatorial positions, which is shown in XXXI.



XXXI

The mass spectrum of $\text{Cl}_3\text{SiFe}(\text{CO})_3\text{NO}$ was reported here in detail in Table XIX. The nitrosyl group was lost after completion of loss of carbonyl groups and the ion, $\text{Cl}_3\text{SiFeNO}^+$ was found as the base peak.

Preparation of $\text{Cl}_3\text{SiFe}(\text{CO})_3\text{NO}$: A solution of $\text{Fe}(\text{CO})_5$ (1.96 g., 10 mmoles) and trichlorosilane (2.0 g., 14.8 mmoles) in 50 ml. of heptane was irradiated for 20 hours at an ambient temperature. The reaction mixture was then cooled to -80° . The cold solvent was decanted off and the vessel refilled with 50 ml. of n-pentane. The yellow solution was cooled to -80° and the cold solvent was decanted, eliminating almost all unreacted trichlorosilane. The vessel was then flushed with nitrogen, leaving a pale-yellow oily solid, $\text{Cl}_3\text{SiFe}(\text{CO})_4\text{H}$, (~ 2.8 g., 85% yield), which was sufficiently pure for preparative purposes. To the vessel containing ~ 2.8 g. of $\text{Cl}_3\text{SiFe}(\text{CO})_4\text{H}$, N-nitroso-N-methyl-p-toluenesulfonamide (2.5 g., 11.7 mmoles) in 50 ml.

TABLE XIX

Mass Spectrum of $\text{Cl}_3\text{SiFe}(\text{CO})_3\text{NO}^*$

m/e ^a	Ion	Relative Abundance
303	$\text{Cl}_3\text{SiFe}(\text{CO})_3\text{NO}^+$	6
275	$\text{Cl}_3\text{SiFe}(\text{CO})_2\text{NO}^+$	105
268	$\text{Cl}_2\text{SiFe}(\text{CO})_3\text{NO}^+$	13
247	$\text{Cl}_3\text{SiFe}(\text{CO})\text{NO}^+$	120
240	$\text{Cl}_2\text{SiFe}(\text{CO})_2\text{NO}^+$	2
219	$\text{Cl}_3\text{SiFeNO}^+$	245
189	Cl_3SiFe^+	180
154	Cl_2SiFe^+	36
133	Cl_3Si^+	18
119	ClSiFe^+	25
91	FeCl^+	40
84	SiFe^+	64
63	SiCl^+	210
56	Fe^+	110

* The source temperature was 5°.

^a m/e values for ³⁵Cl-containing ions

of diethyl ether was added and the solution was stirred at room temperature for one hour. The reaction mixture was then transferred to a 300 ml. flask and volatiles were removed under reduced pressure. The orange crystalline $\text{Cl}_3\text{SiFe}(\text{CO})_3\text{NO}$ was sublimed out of the residue at $20-30^\circ/0.1$ mm. onto a probe cooled by dry ice-acetone (1.2 g. , ~ 40% yield based on $\text{Cl}_3\text{SiFe}(\text{CO})_4\text{H}$ employed). Attempts to obtain $\text{Ph}_3\text{SiFe}(\text{CO})_3\text{NO}$ by the reaction of $\text{Ph}_3\text{SiFe}(\text{CO})_4\text{H}$ and Diazald resulted in the formation of $\text{Fe}(\text{CO})_2(\text{NO})_2$.

4. Preparation and properties of $\text{Co}_3(\text{CO})_{10}\text{BHNMe}_2\text{BH}_2\text{NMe}_2$

INTRODUCTION

Silicon hydrides have been shown to react with dicobalt octacarbonyl to produce the silicon-cobalt bond as the following reaction shows:



R = Ph, Et, Cl, etc.

It seemed that boron-hydrogen bonds in a suitable compound such as $(\text{Me}_2\text{NBH}_2)_2$ could be reactive towards dicobalt octacarbonyl. Described here is the rather unexpected compound isolated in the course of investigation of the above possibility. Almost concurrently with the isolation of the titled compound in the present work, Klanberg, Askew and Guggenberger reported very similar compounds obtained while exploring the possibility of incorporating a boron atom (or a BH group) into a $\text{Co}_3(\text{CO})_9$ cluster by treatment of trialkylamine-boranes with dicobalt octacarbonyl (153).

RESULTS AND DISCUSSION

Dimethylaminoborane dimer, $(\text{Me}_2\text{NBH}_2)_2$, reacted with dicobalt octacarbonyl in hydrocarbon solvents to produce a compound of composition $\text{Co}_3(\text{CO})_{10}\text{B}_2\text{N}_2\text{H}_3\text{Me}_4$. This compound was a red-violet crystalline solid, which was stable

to air at room temperature, and melted at 78° with decomposition. The observed infrared spectrum in the carbonyl stretching region was virtually identical with those of $\text{Co}_3(\text{CO})_9\text{CX}$ (where $\text{X} = \text{Cl}, \text{H}, \text{Me}$ etc.), exhibiting bands at $2098(\text{w}), 2043(\text{vs}), 2032(\text{s})$ and $2010(\text{m}) \text{ cm}^{-1}$ in cyclohexane. This suggested the presence of a $\text{Co}_3(\text{CO})_9$ cluster in the molecule.

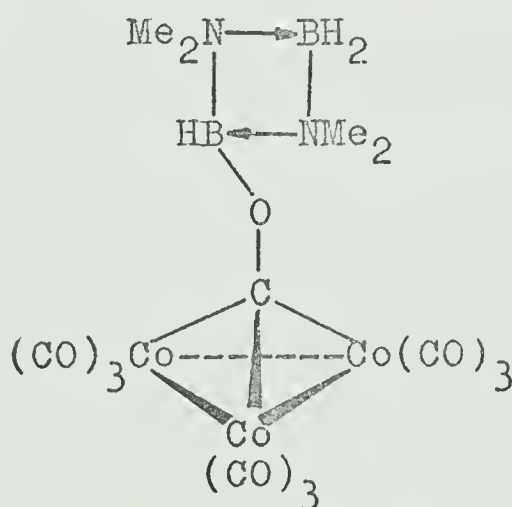
Evidence for the presence of BH and BH_2 groups in the molecule was obtained from a doublet superimposed on a triplet in the ^{11}B NMR spectrum which is shown in Figure 20. The doublet centered at -8.15 ppm and the triplet centered at -3.81 ppm from Et_2OBF_3 external reference ($J_{\text{BH}(\text{BH})} = J_{\text{BH}(\text{BH}_2)} = 122$ cps). These values may be compared with the triplet exhibited by $(\text{Me}_2\text{NBH}_2)_2$ at -3.7 ppm ($J_{\text{BH}} = 116$ cps) from the same reference. A rather low field doublet may be attributed to the weaker shielding of the boron nucleus due to its proximity to an electronegative oxygen atom. The proton spectrum showed a broad resonance at τ 7.50 superimposed on humps due to resonances of BH and BH_2 groups in CCl_4 . The separation of the latter broad resonances was roughly 120-125 cps.

The mass spectrum of the compound was highly complex, unlike those obtained for $\text{Co}_3(\text{CO})_9\text{CX}$ (where $\text{X} = \text{Cl}, \text{Me}$) (95). Whilst ions corresponding to the stepwise loss of nine carbonyl groups from the molecular ion were unequivoc-



FIGURE 20. The ^{11}B NMR spectrum of $\text{Co}_3(\text{CO})_{10}\text{BHNMe}_2\text{BH}_2\text{NMe}_2$

ally identified, the spectrum did not provide evidence for the mode of bonding of the tenth carbonyl group. A similar phenomenon was reported in the mass spectra of $\text{Co}_3(\text{CO})_{10}\text{BH}_2\text{NR}_3$ (where $\text{R} = \text{Me}, \text{Et}$) (153). However, the crystal structure of $\text{Co}_3(\text{CO})_{10}\text{BH}_2\text{NEt}_3$ (153) evidently shows one unique carbonyl group triply bridging three cobalt atoms, actually unlike those found in $(\text{C}_5\text{H}_5)_3\text{Ni}(\text{CO})_2$ (154), $\text{Rh}_6(\text{CO})_{16}$ (155) etc. It appeared that this was the case for the compound discussed here, thus the structure XXXII is postulated from a consideration of all of the spectroscopic data.



XXXII

Preparation of $\text{Co}_3(\text{CO})_{10}\text{BHNMe}_2\text{BH}_2\text{NMe}_2$: Dicobalt octacarbonyl (1.14 g., 3 mmoles) and $(\text{Me}_2\text{NBH}_2)_2$ (prepared by heating Me_2NHBH_3 at $250 - 300^\circ$ in an electric furnace)

(0.56 g., 5 mmoles) in 20 ml. of hexane were sealed in an evacuated Carius tube at liquid nitrogen temperature. The tube was then heated at 95° for two hours with mechanical shaking. The deep red-brown reaction mixture was cooled to -80° to afford a dark red-violet powder. This was recrystallized from n-pentane (0.6 g., 35% yield based on $\text{Co}_2(\text{CO})_8$ employed).

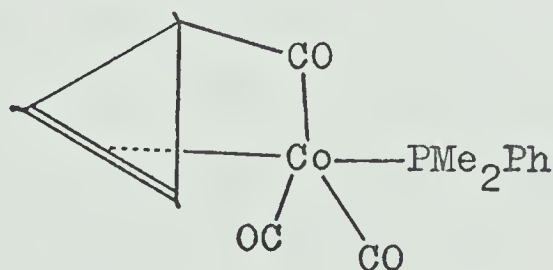
5. Preparation and properties of dimethylphenylphosphine derivatives of 1,2,3-triphenylcyclopropenylcobaltcarbonyl.

INTRODUCTION

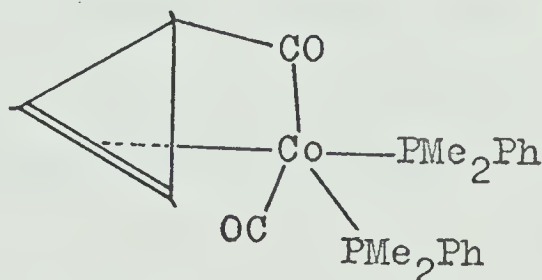
As mentioned in Chapter I, triphenylcyclopropenyl halide reacts with $\text{Co}(\text{CO})_4^-$ to produce $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_4$ which contains a unique carbonyl group believed to be bridging the ring and the cobalt atom (29). The reaction of the latter compound with dimethylphenylphosphine was described here.

RESULTS AND DISCUSSION

The reaction between $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_4$ and PMe_2Ph resulted in the isolation of the monophosphine compound, $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_3\text{PMe}_2\text{Ph}$ (XXXIII), and the bisphosphine compound, $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})_2$ (XXXIV). In both compounds, the ring



XXXIII



XXXIV

moiety appeared to be bonded to the cobalt atom by a ketonic carbonyl group and a double bond of the ring (π -bond).

The infrared spectrum of the monophosphine compound showed carbonyl stretching bands (in cyclohexane solution) at 2029(s), 2024(s), 1986(s), 1981(s) and 1685 cm^{-1} . The proton NMR spectrum exhibited a sharp doublet at τ 8.34 ($J_{\text{PCH}_3} = 8.34$ cps) (methyl group) and a multiplet at τ 2.70 (phenyl group). The four terminal carbonyl stretching bands, together with the NMR data suggested that there were conformational isomers. These are most likely to be rotational isomers with respect to the Co—P bond. This type of effect of unsymmetrically substituted group on the terminal carbonyl stretching frequencies was discussed in detail in Chapter III.

The infrared spectrum of the bisphosphine compound showed two bands at 1951(s) and 1649(s) cm^{-1} in the carbonyl stretching region (in methylene chloride solution). The 60 Mc. NMR spectrum exhibited a quartet in the CH_3 region, centered at τ 8.82, with unequal intensities. However, the latter resulted in a triplet (intensities 1 : 2 : 1) in the 100 Mc. spectrum (CDCl_3 solution). This is shown in Figure 21.

The mass spectra of these compounds including $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_4$, were particularly interesting. In addition

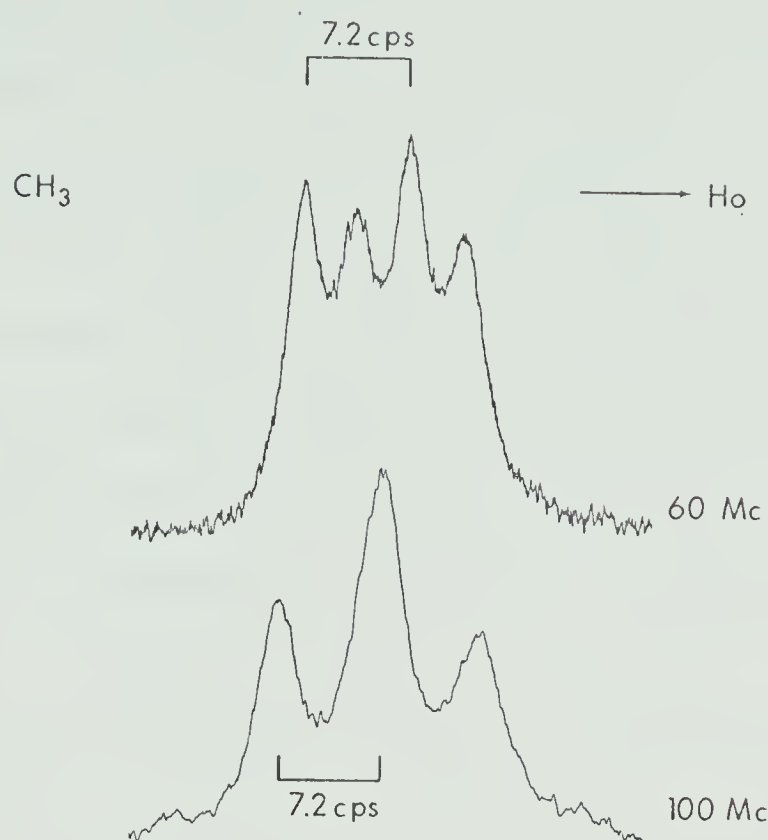


Figure 21. The methyl resonance of the phosphine groups in $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})_2$.

to the ions due to consecutive loss of carbonyl groups from the molecular ions, all the mass spectra exhibited fragments corresponding to $\text{Ph}_6\text{C}_6\text{Co}_2(\text{CO})_n^+$ (where $n = 2, 1, 0$), and $\text{Ph}_6\text{C}_6\text{Co}^+$ and Ph_6C_6^+ . A similar phenomenon was reported in the mass spectrum of $\text{Me}_3\text{C}_3\text{Co}(\text{CO})_4$ (30). These ions constituted all the intense peaks in the mass spectrum of the bisphosphine derivative. As the sample was heated to 180° in the inlet system, these fragments became more intense. In the mass spectrum of the monophosphine der-

ivative, the ion which had lost three carbonyl groups from the molecular ion was the base peak. This was also found in the mass spectrum of $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_4$, while the ion, Ph_6C_6^+ , was found as the base peak in the bisphosphine derivative. The occurrence of the peak corresponding to Ph_3C_3^+ ion and absence of the fragment corresponding to $\text{Ph}_3\text{C}_4\text{O}^+$ together with the above data can possibly be invoked as evidence of the mode of attachment of the ring moiety. From the infrared data alone, this remained ambiguous and structures VI and VII (Chapter I) were suggested (29). The above observation is in agreement with the structure VI, although the structure VII was suggested for the permethyl derivative (30).

All of the compounds described here failed to release carbon monoxide after being irradiated by ultraviolet light for 15 hours.

Preparation of $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_3\text{PMe}_2\text{Ph}$ and $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_2^-(\text{PMe}_2\text{Ph})_2$: A solution of 1.1 g. (2.5 mmoles) of $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_4$ (prepared by the method described by Coffey (29)) and 0.35 g. (2.5 mmoles) of dimethylphenylphosphine in 50 ml. of hexane was heated at refluxing temperature for 15 hours. The reaction mixture was allowed to cool to room temperature. An orange precipitate was filtered, and the filtrate was concentrated to a small volume to afford more orange precipitate. This was filtered. The

filtrate was kept standing at room temperature for about 20 hours, to produce orange-yellow crystals. These were recrystallized from n-pentane to afford analytically pure $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_3\text{PMe}_2\text{Ph}$ (0.22 g., 16% yield). The combined orange precipitate was dissolved in minimum amount of methylene chloride, filtered, and n-pentane was added. The solution was cooled to -20° to afford orange crystals of $\text{Ph}_3\text{C}_3\text{Co}(\text{CO})_2(\text{PMe}_2\text{Ph})_2$ (0.40 g., 36% yield).

INFRARED SPECTRA

All spectra presented in the following pages were measured in cyclohexane solutions unless otherwise denoted.

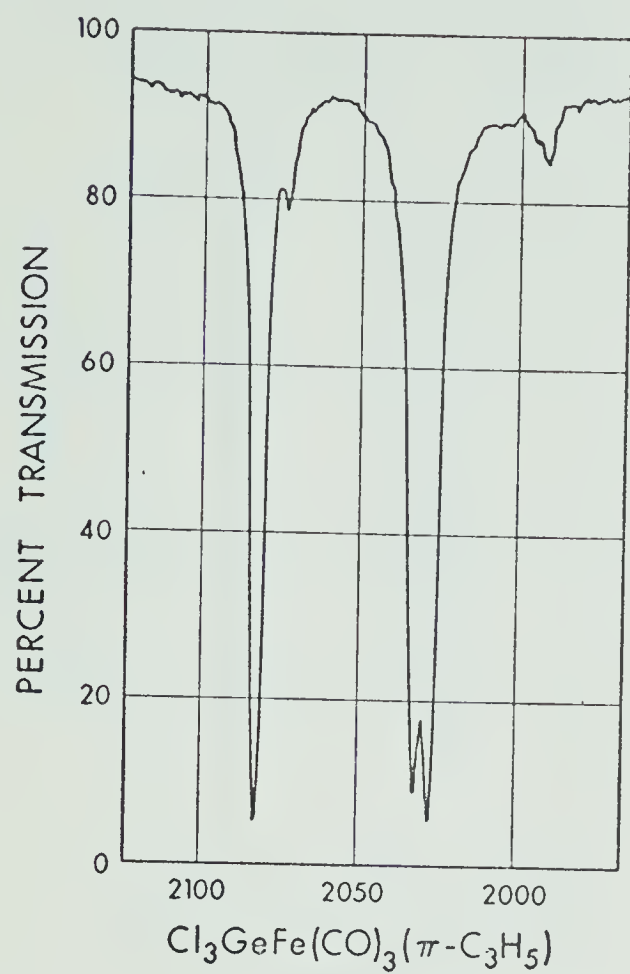


FIGURE 22

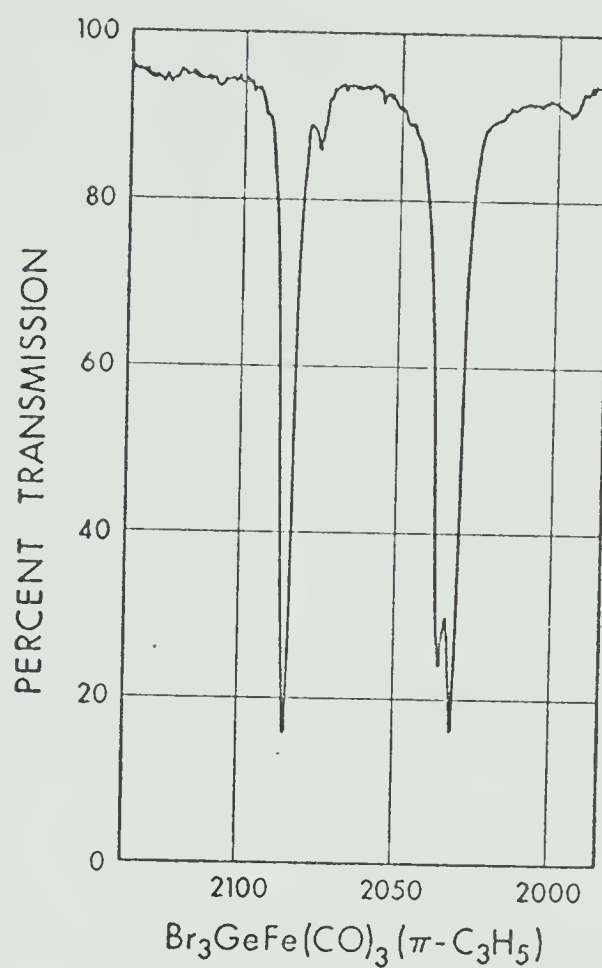


FIGURE 23

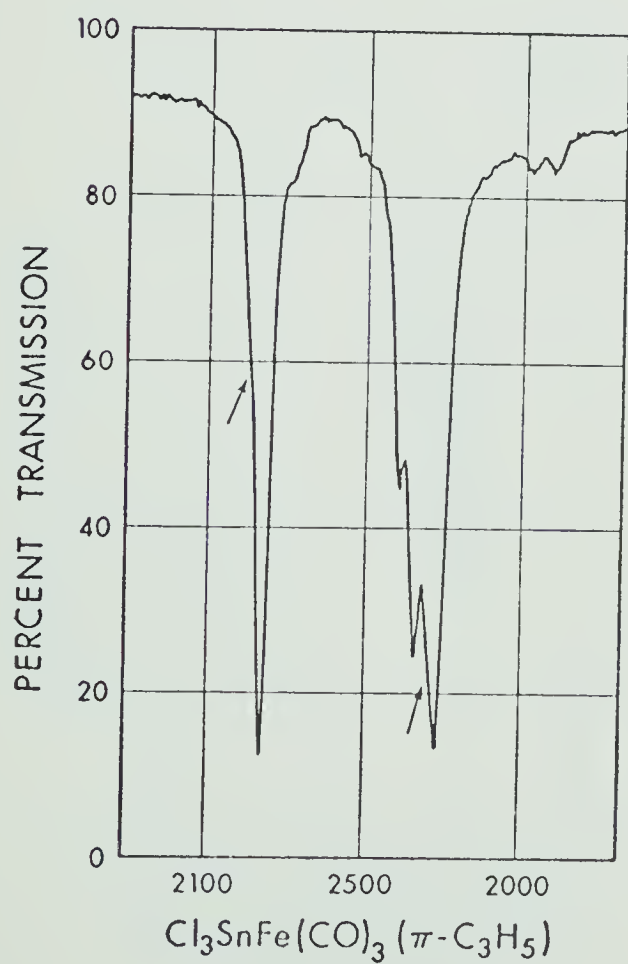


FIGURE 24

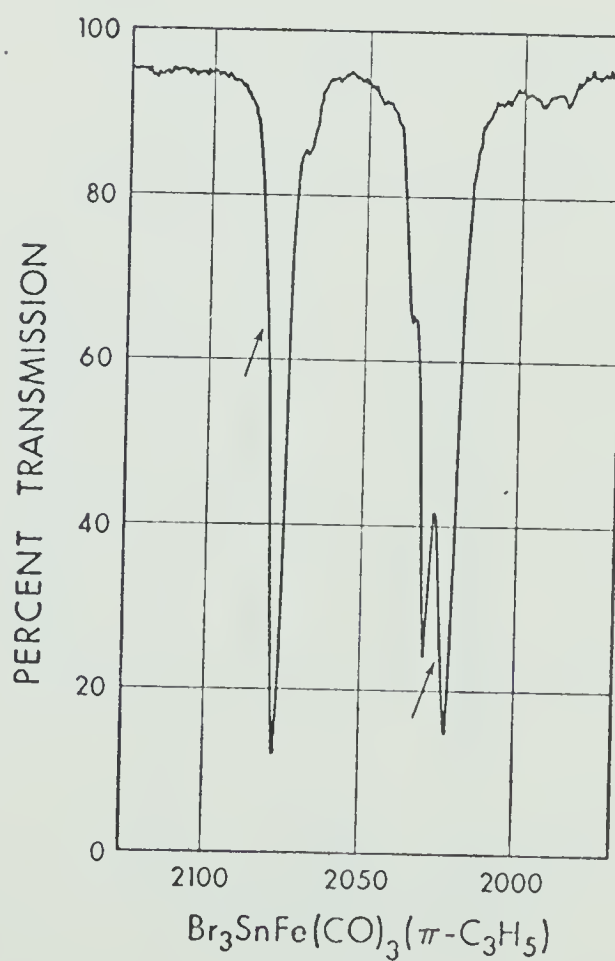


FIGURE 25

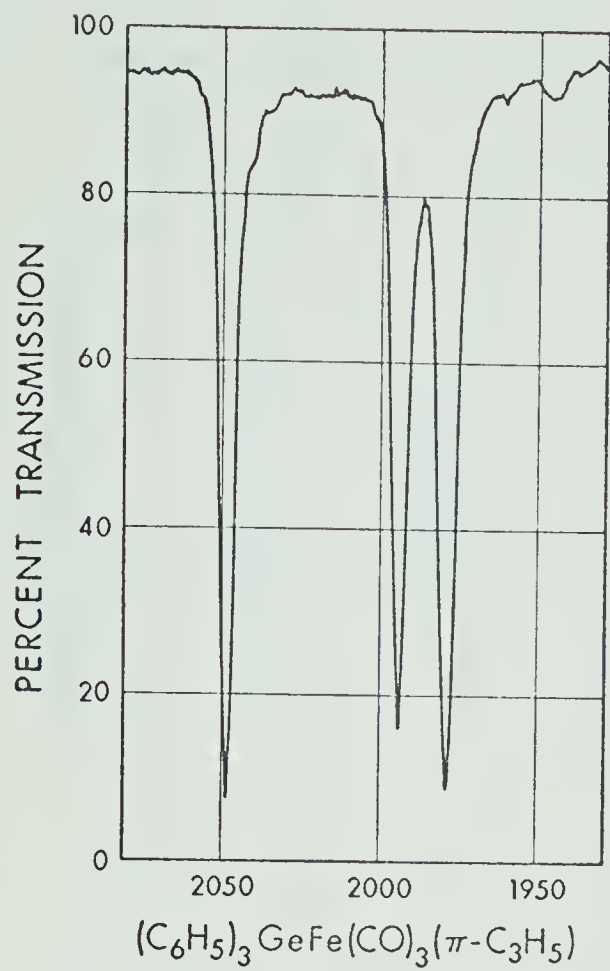


FIGURE 26

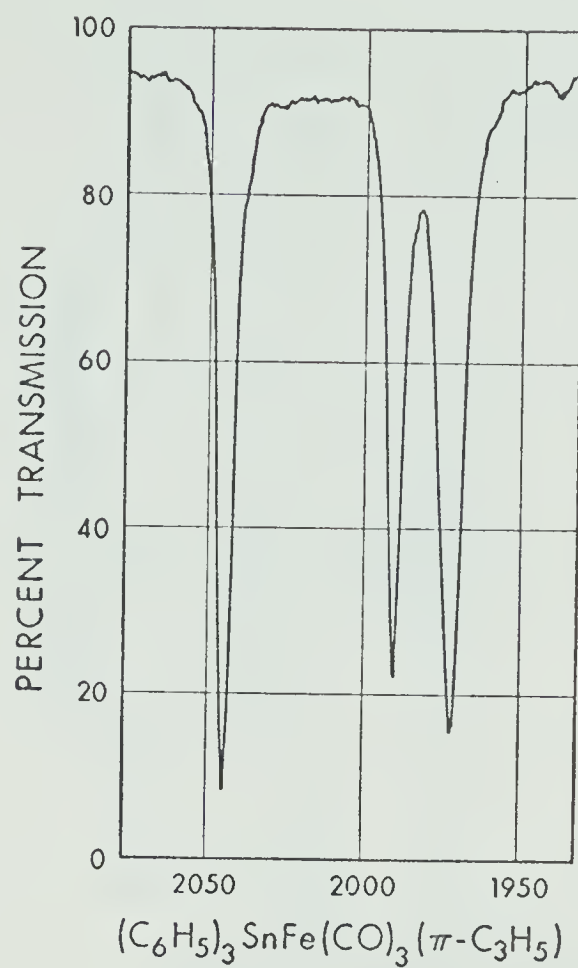


FIGURE 27

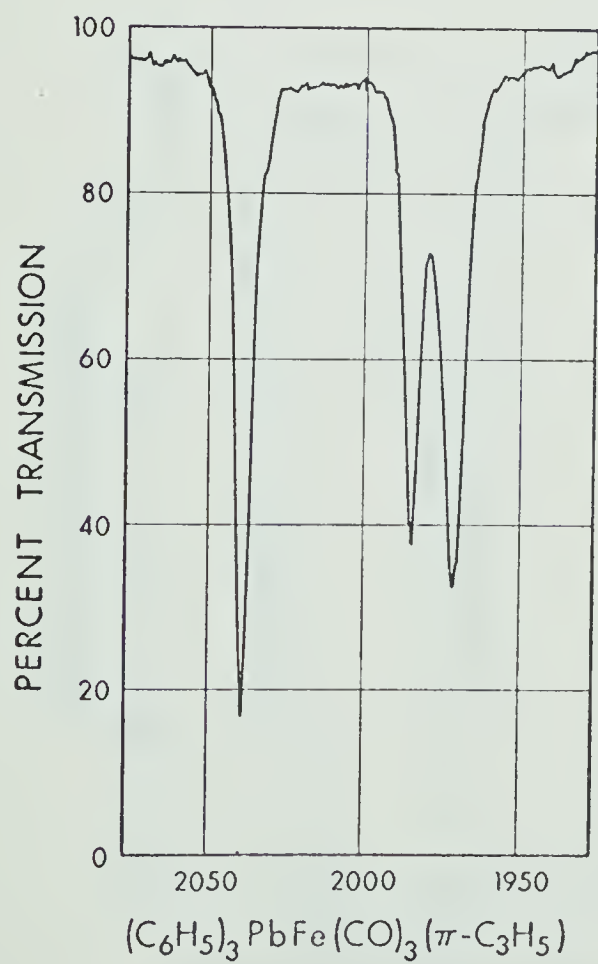


FIGURE 28

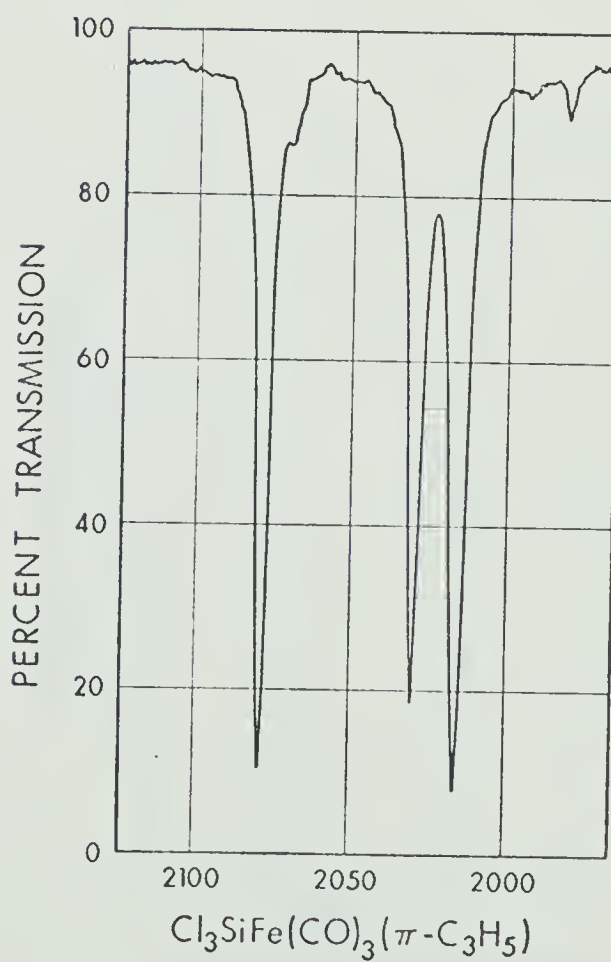


FIGURE 29

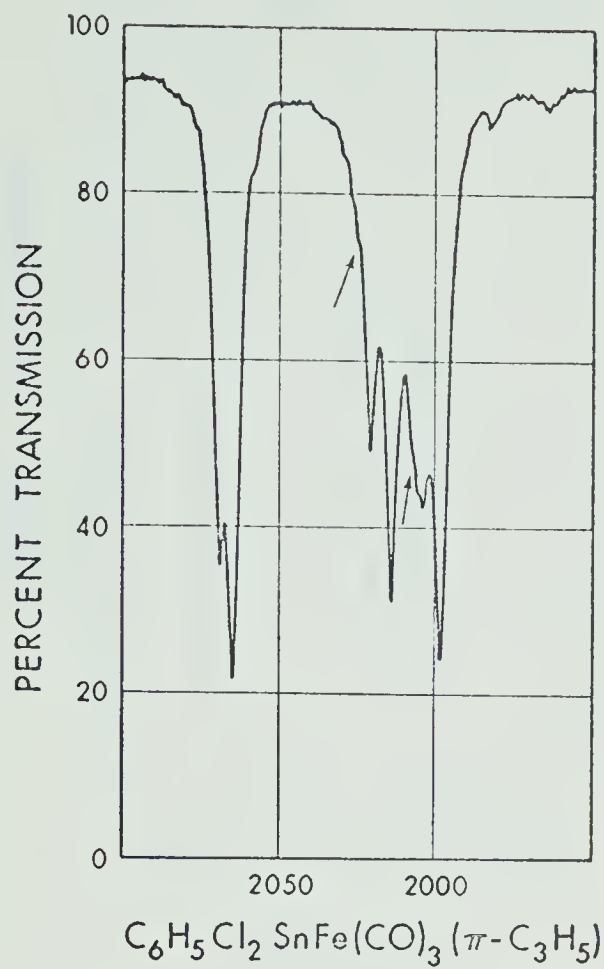


FIGURE 30

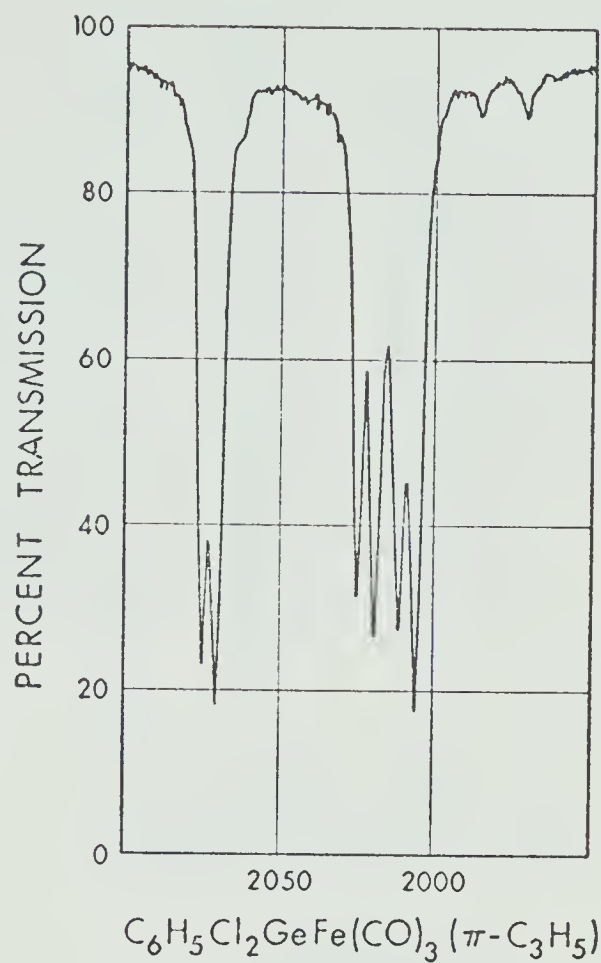


FIGURE 31

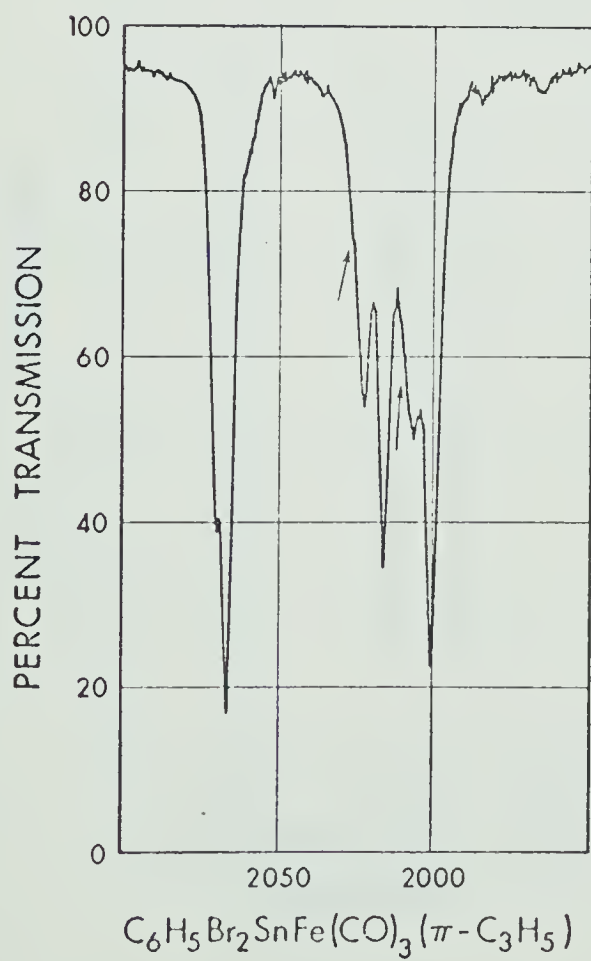


FIGURE 32

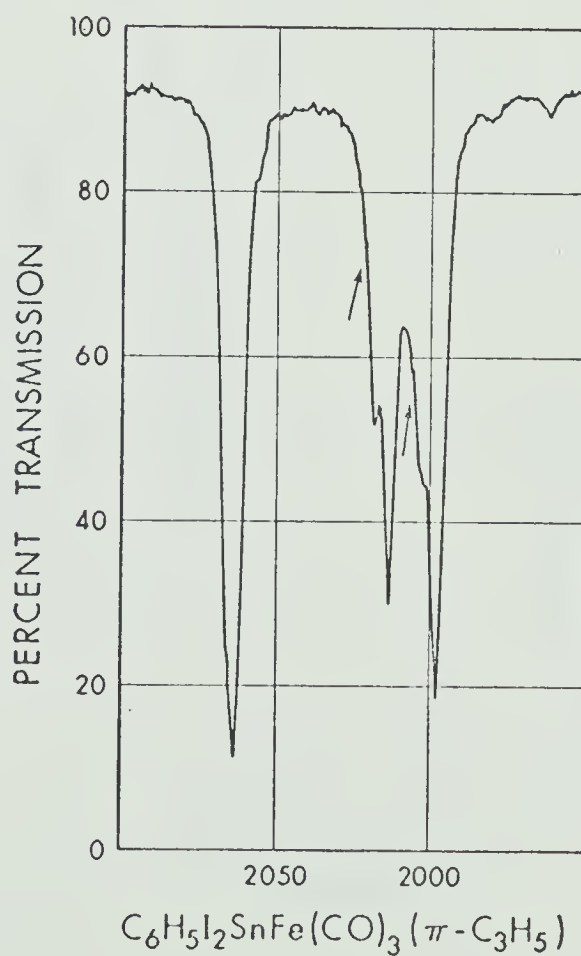


FIGURE 33

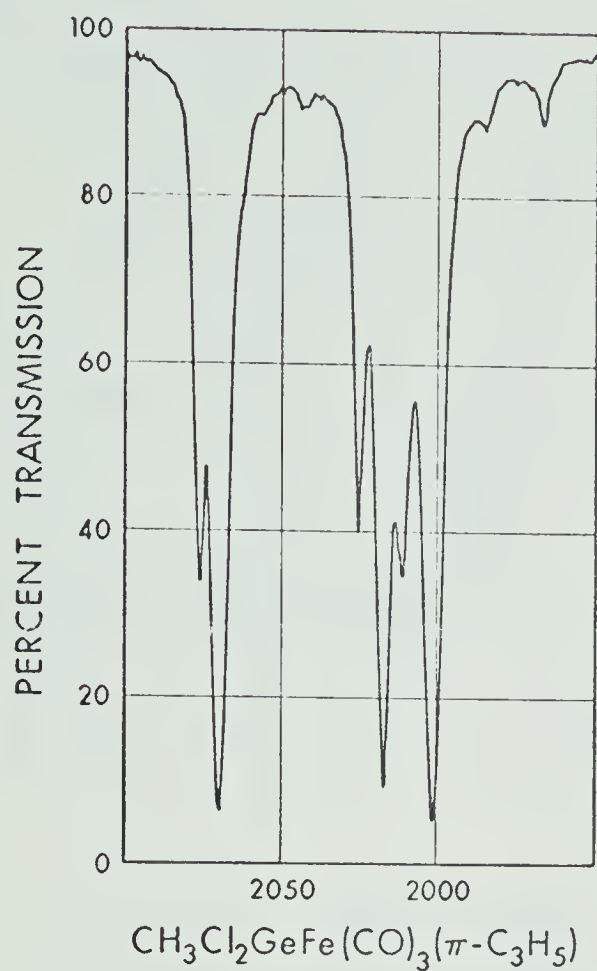


FIGURE 34

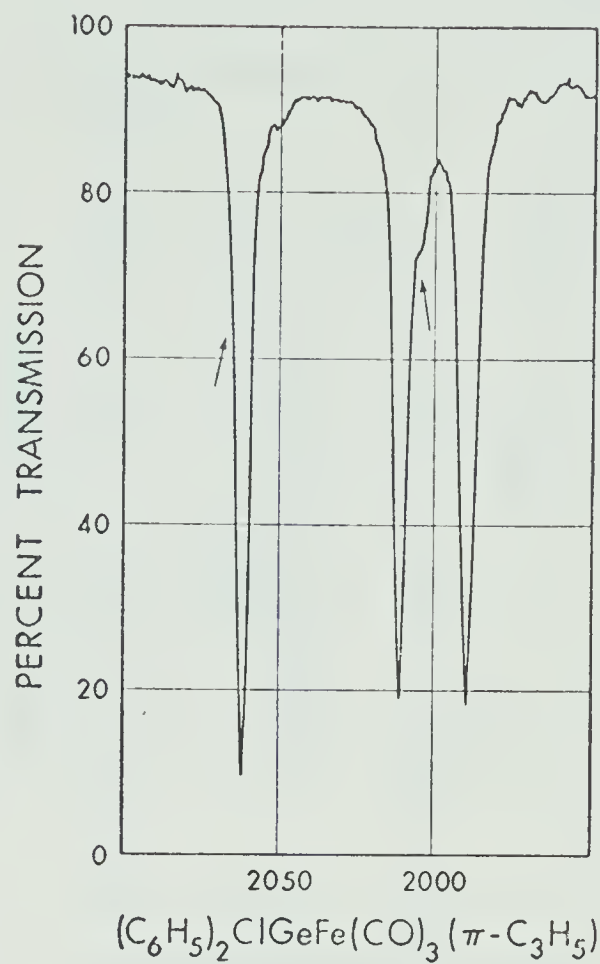


FIGURE 35

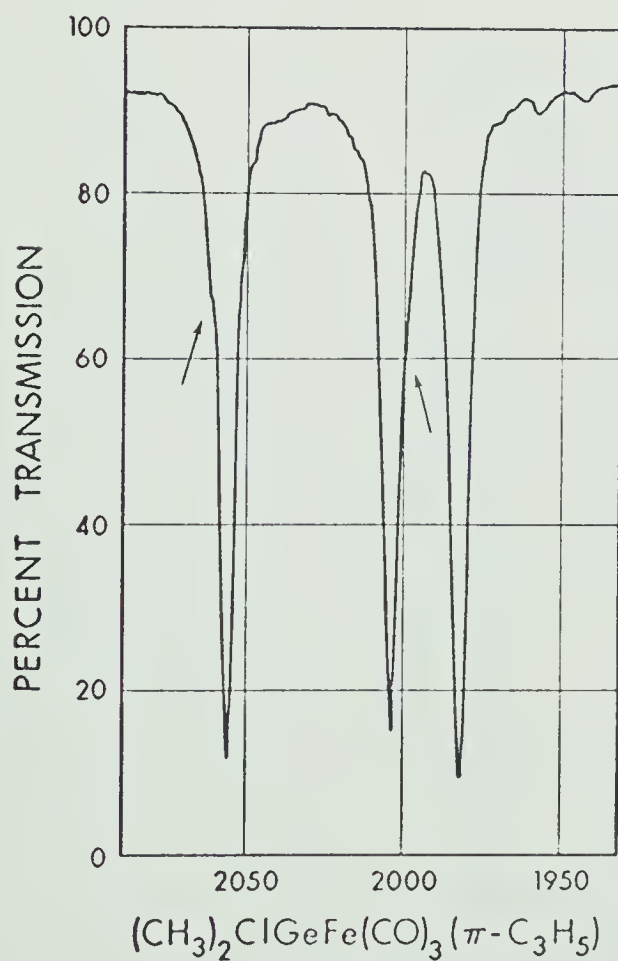


FIGURE 36

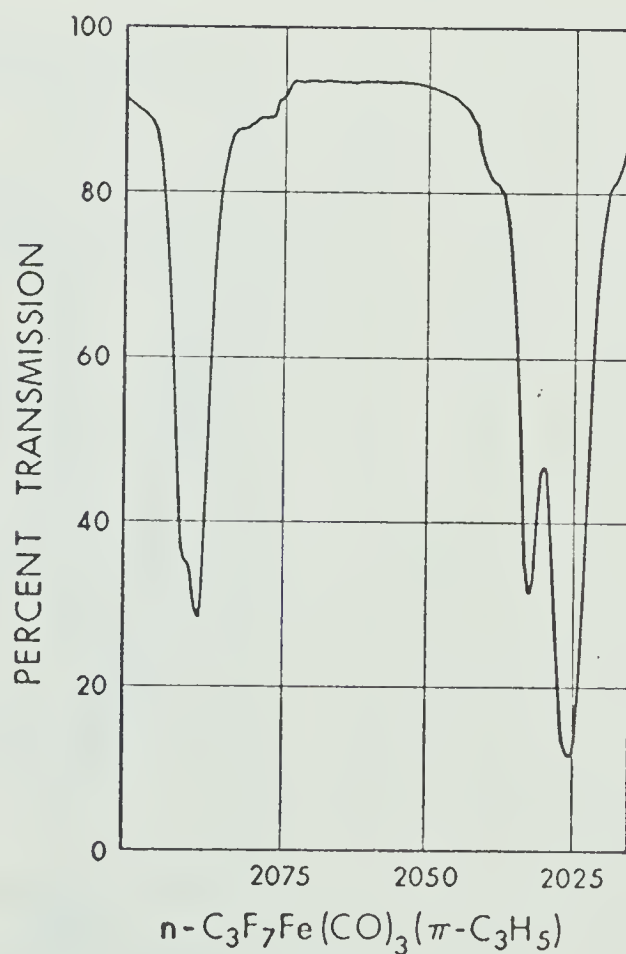


FIGURE 37

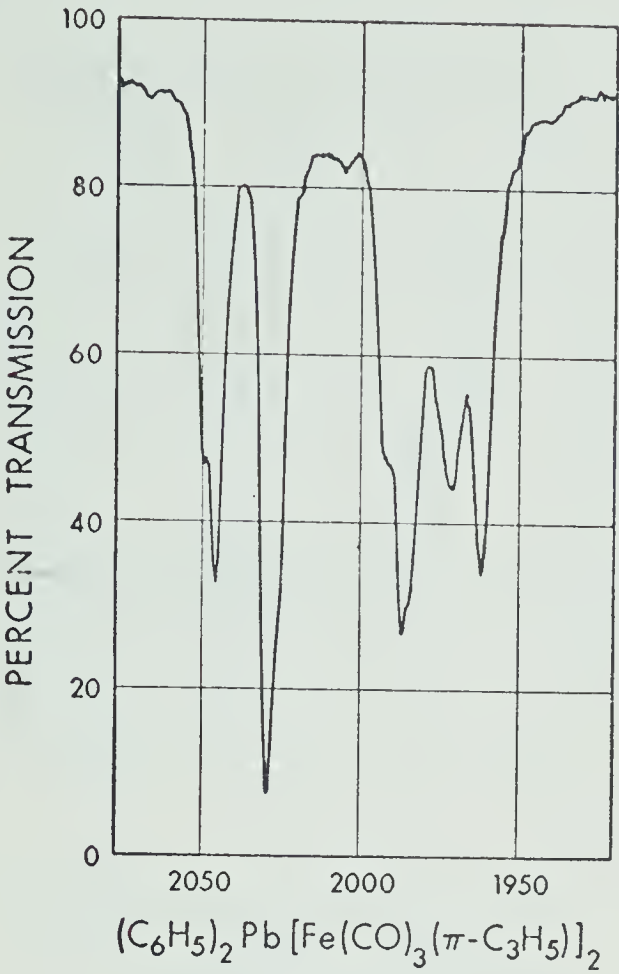


FIGURE 38

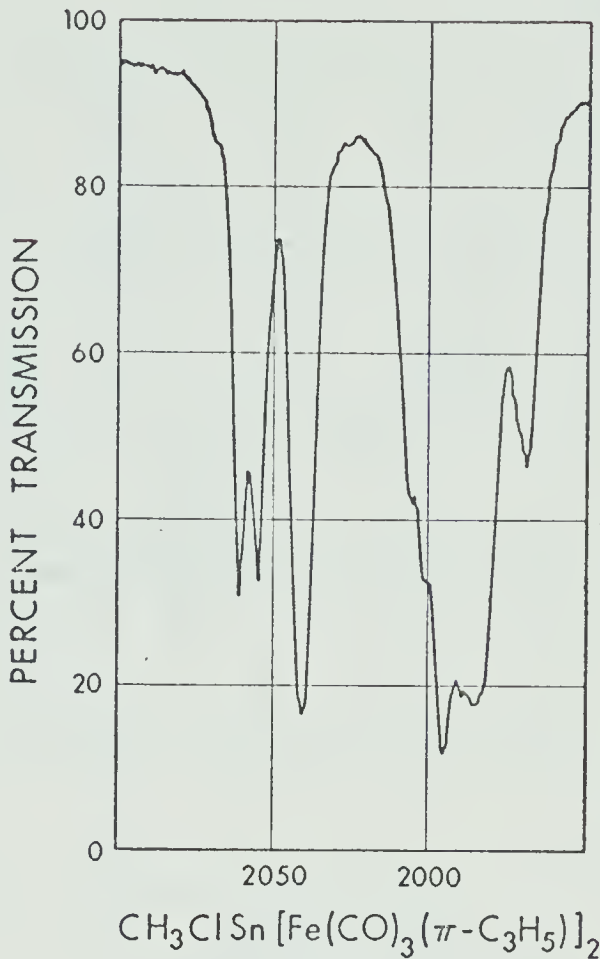


FIGURE 39

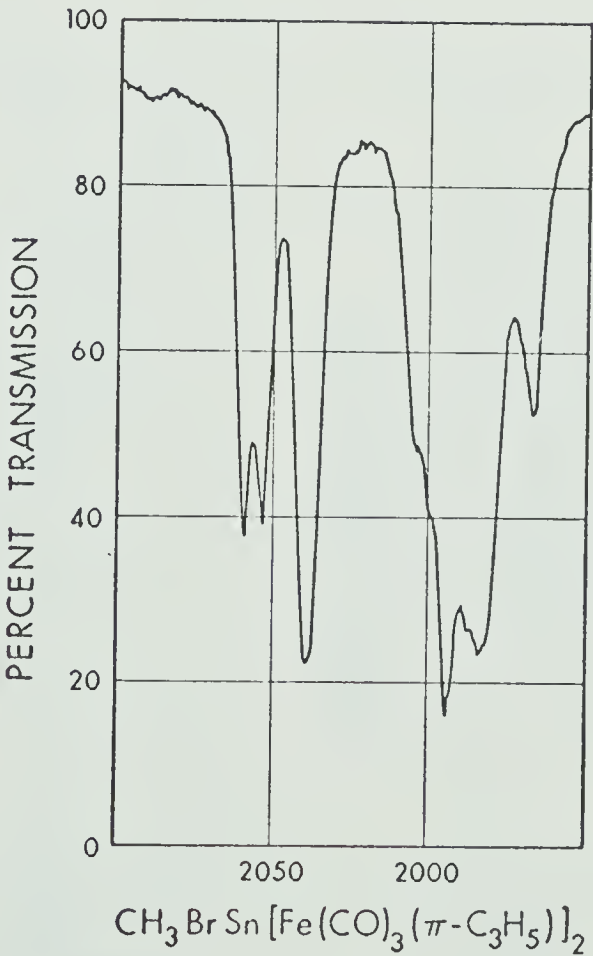


FIGURE 40

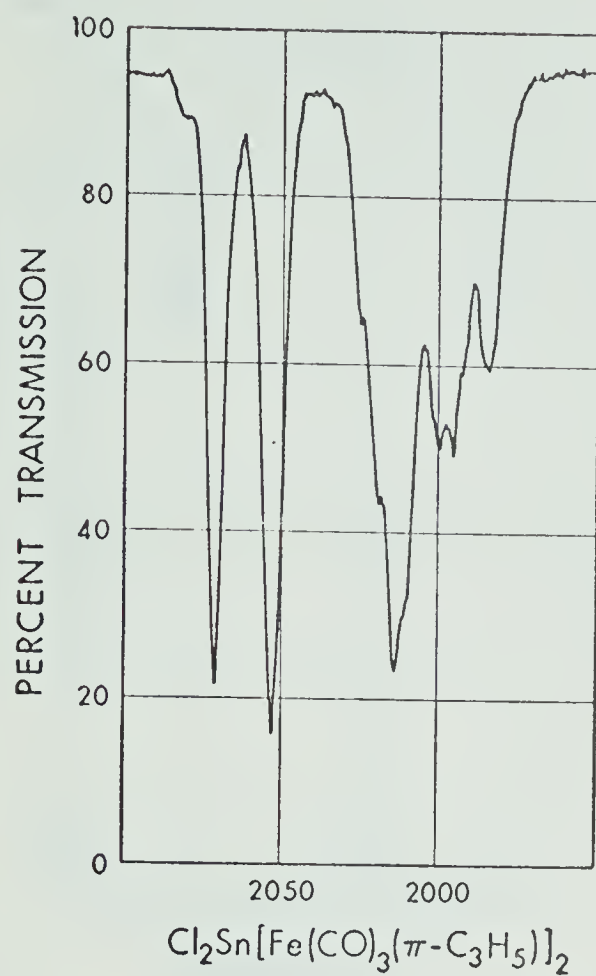


FIGURE 41

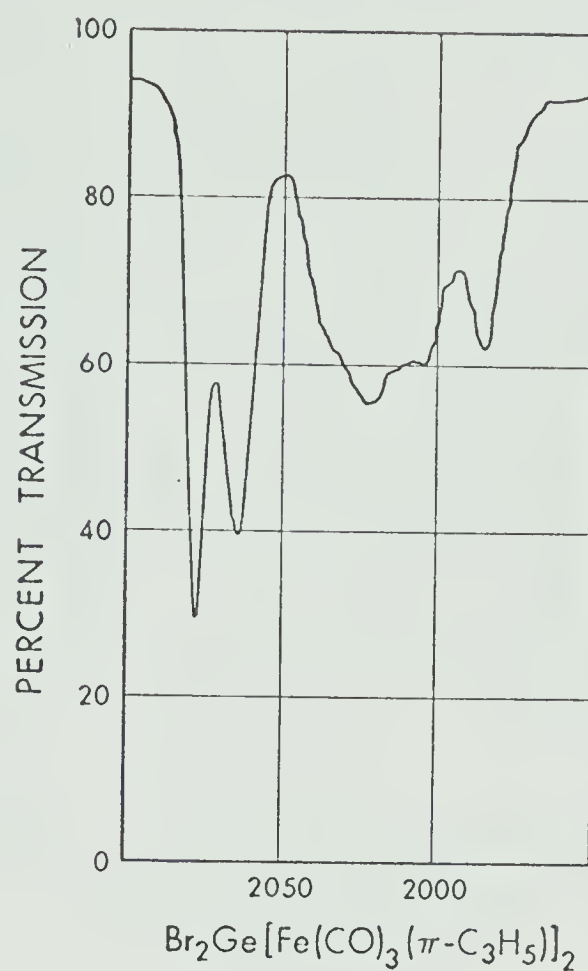


FIGURE 42

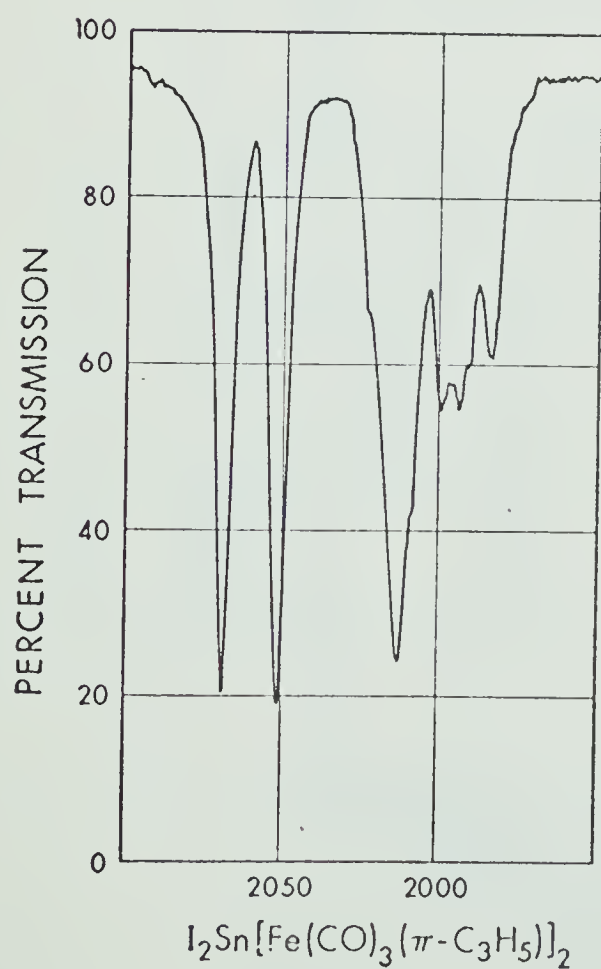


FIGURE 43

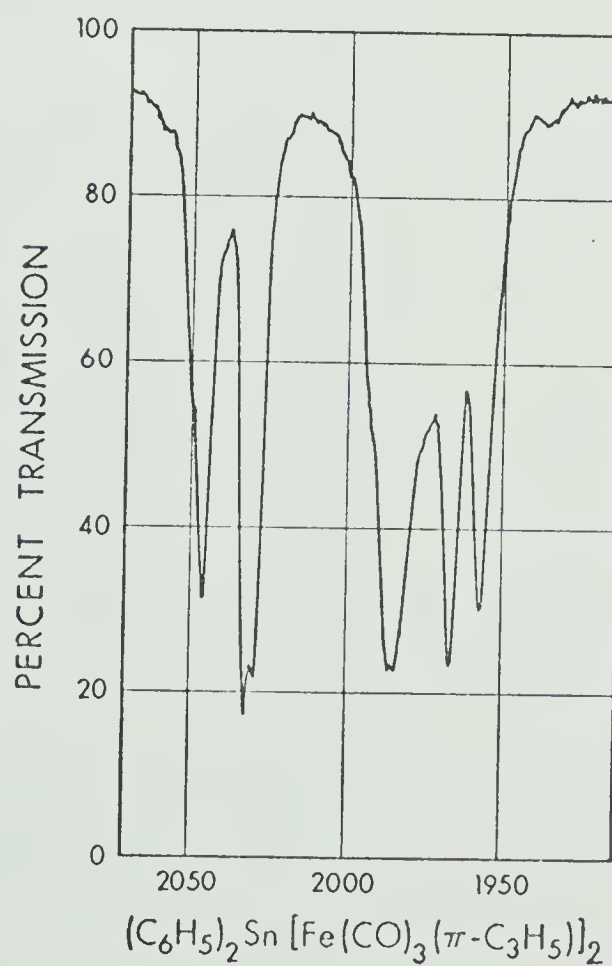


FIGURE 44

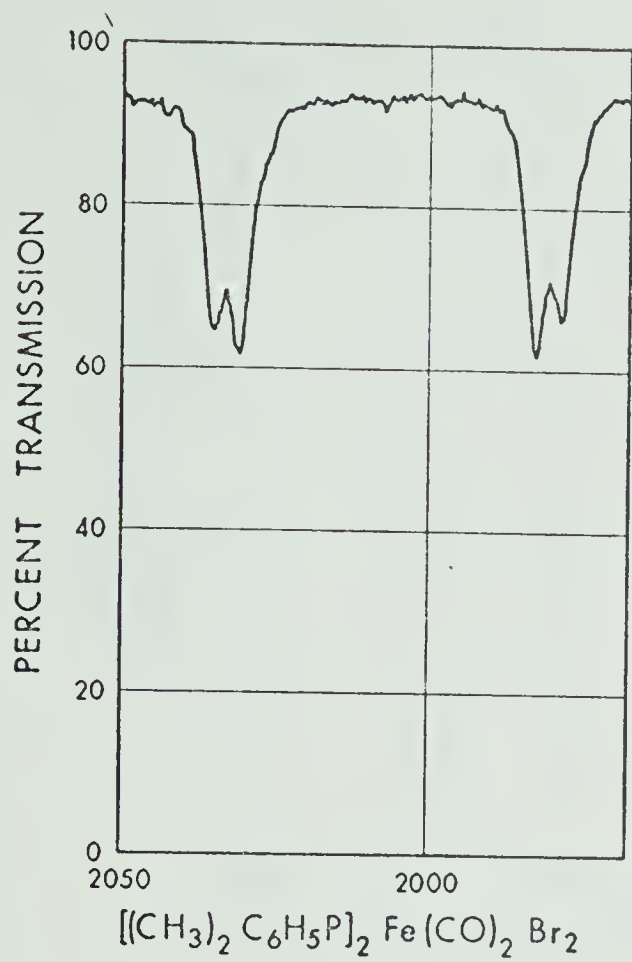


FIGURE 45

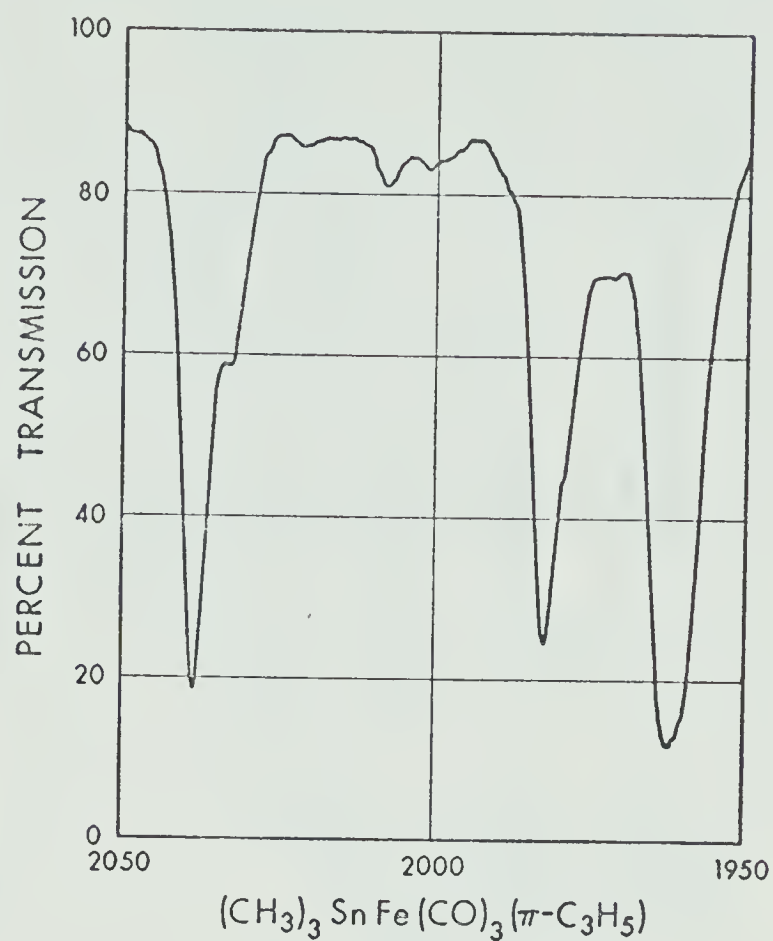


FIGURE 46

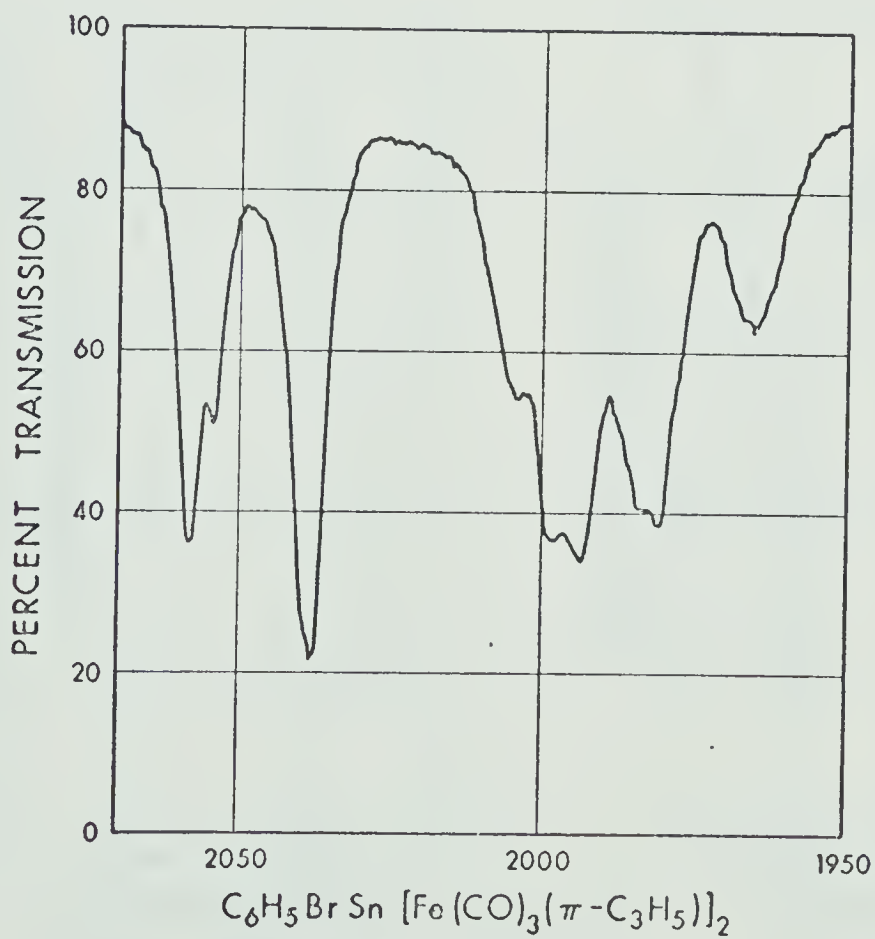


FIGURE 47

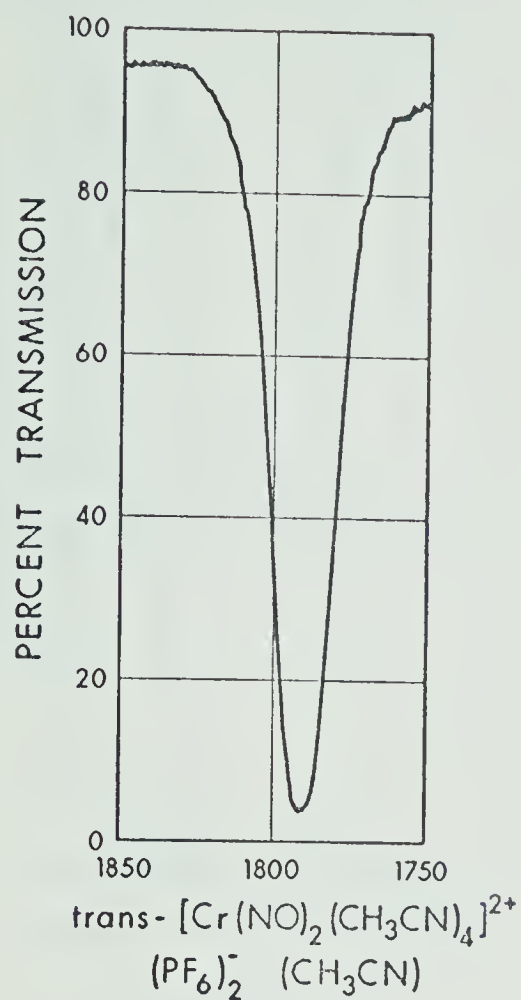


FIGURE 48

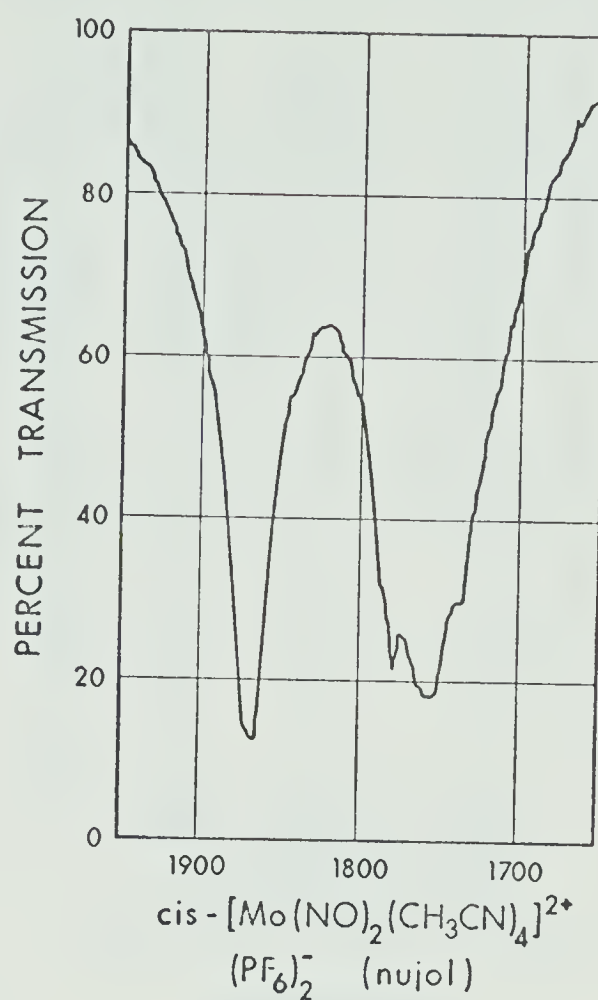


FIGURE 49

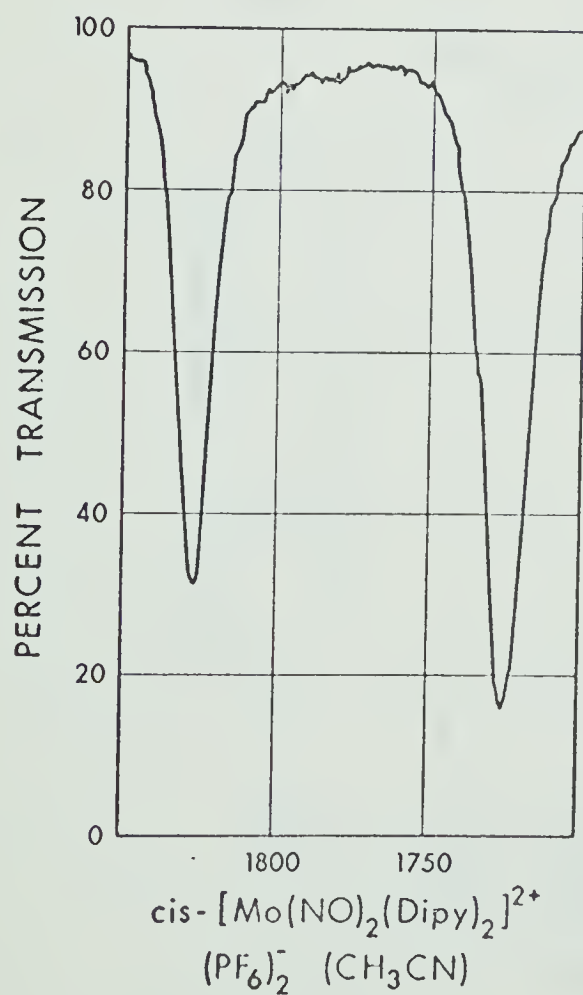


FIGURE 50

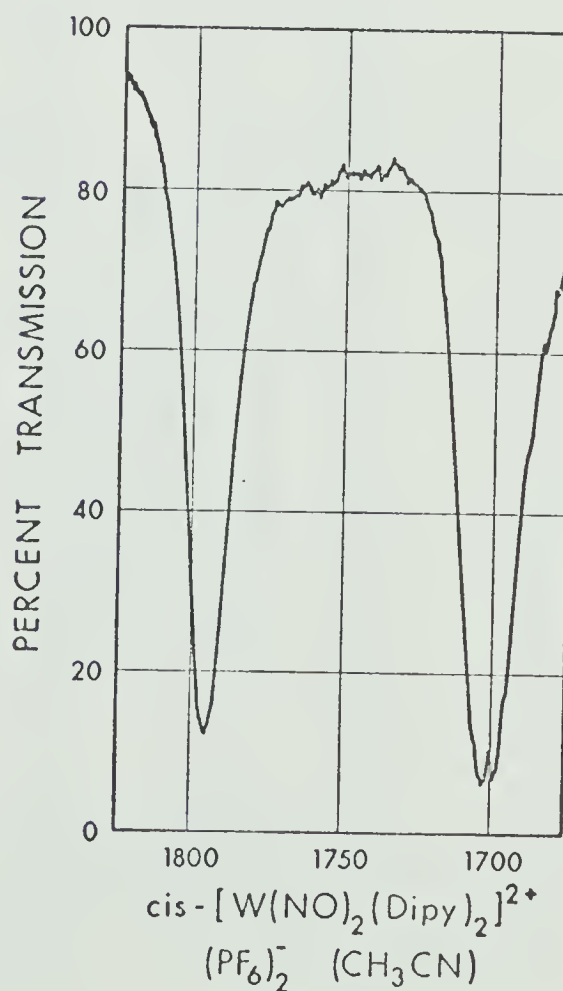


FIGURE 51

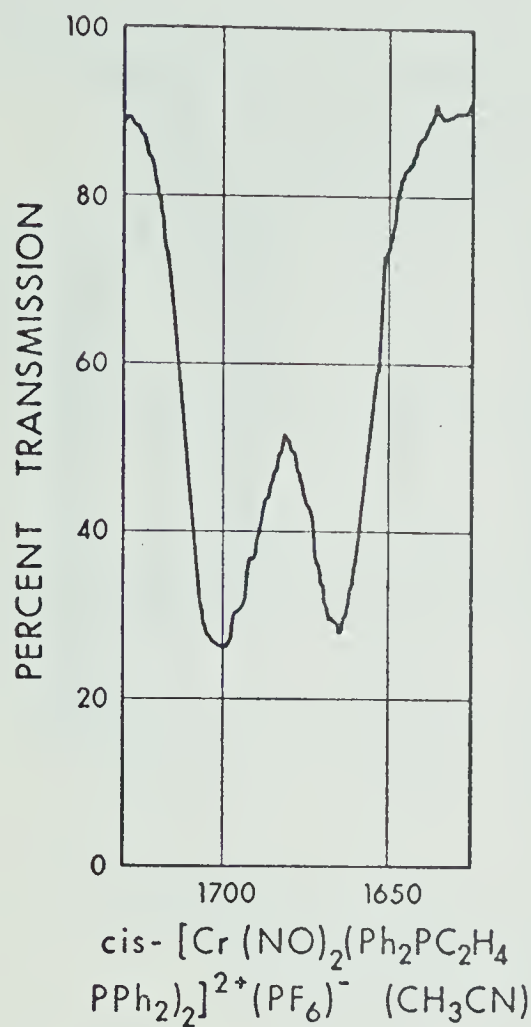


FIGURE 52

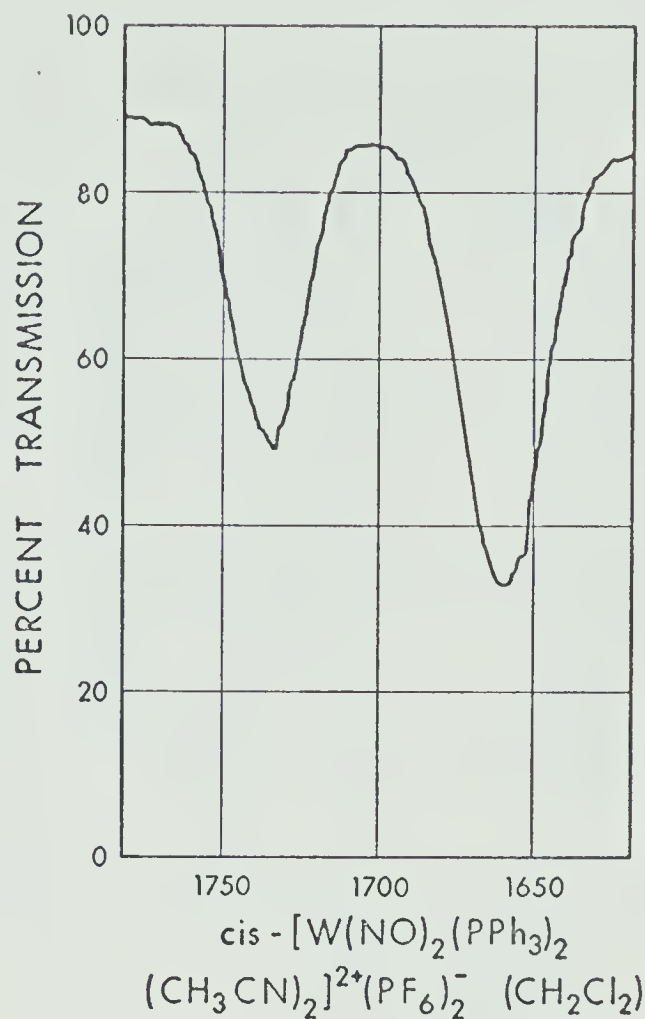


FIGURE 53

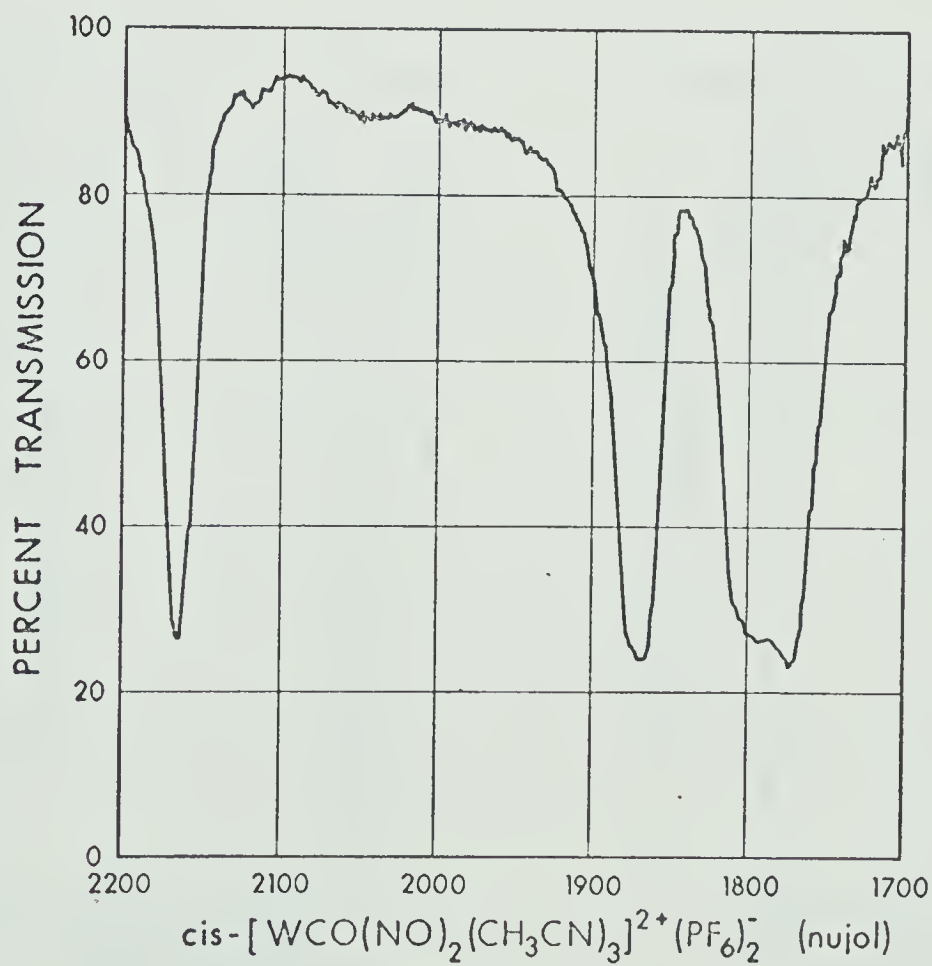
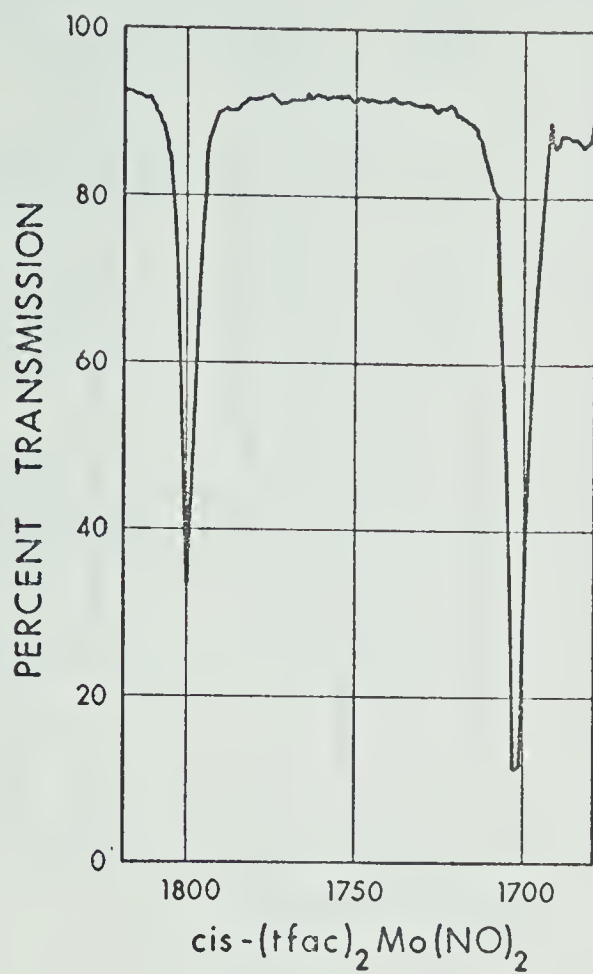
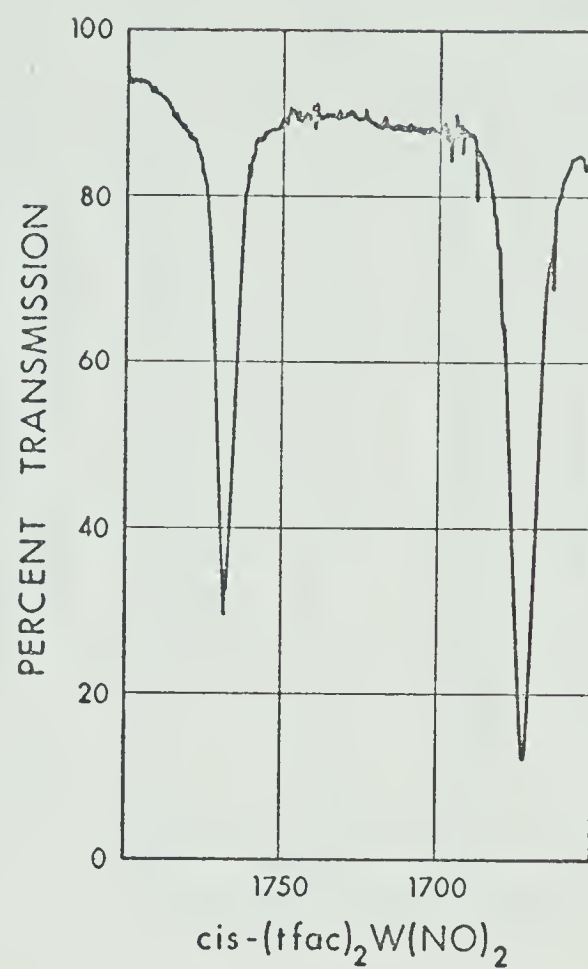
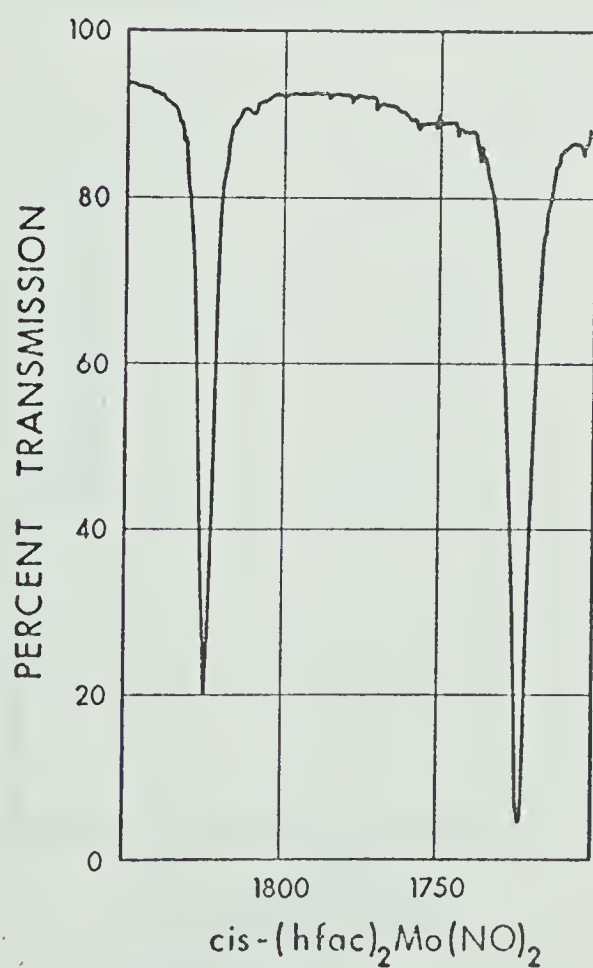
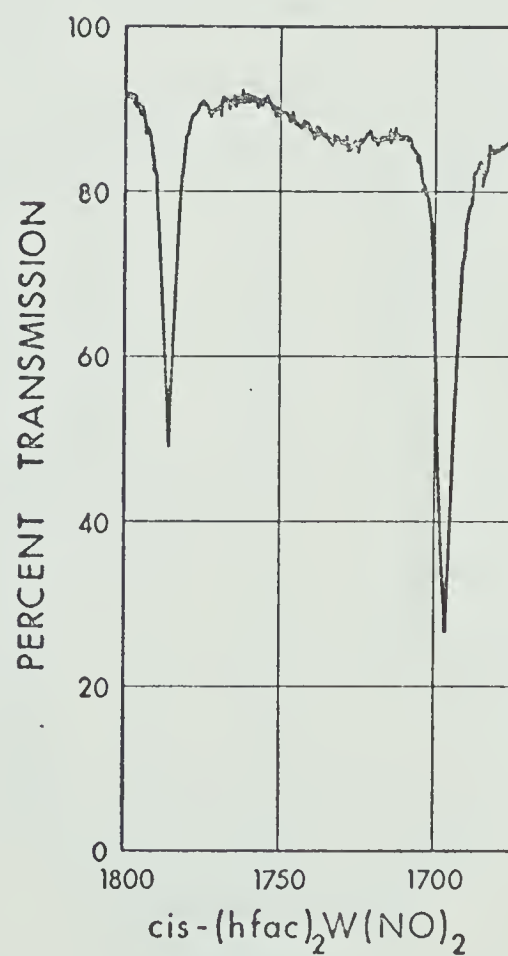


FIGURE 54

FIGURE 55FIGURE 56FIGURE 57FIGURE 58

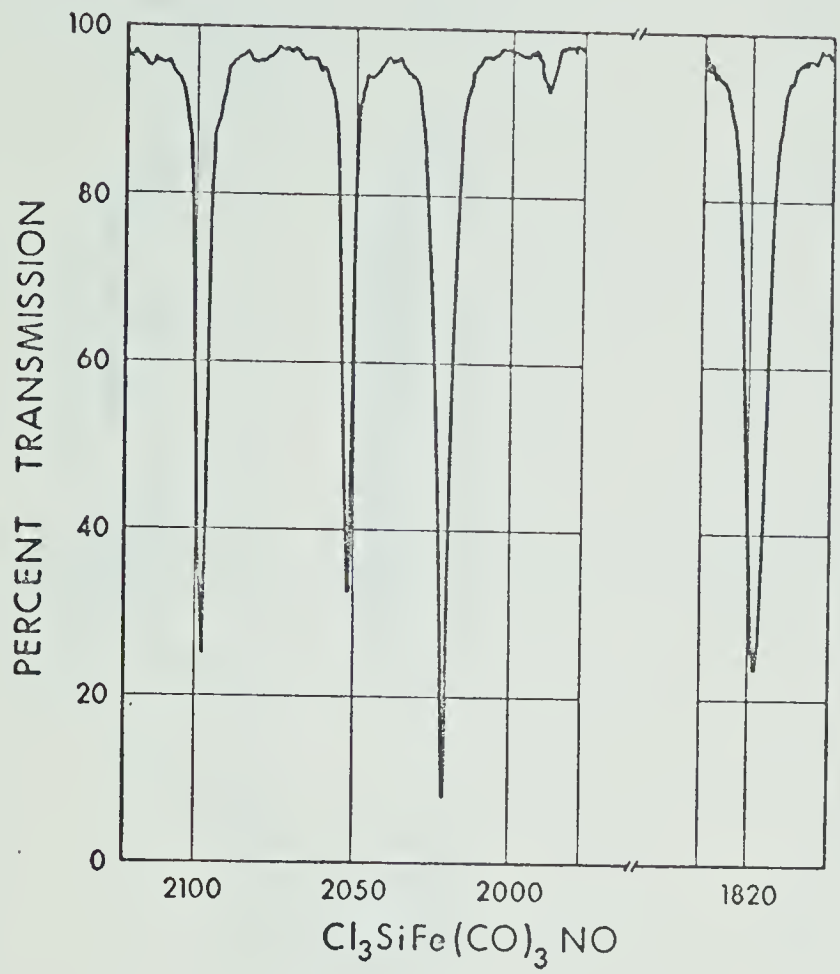


FIGURE 59

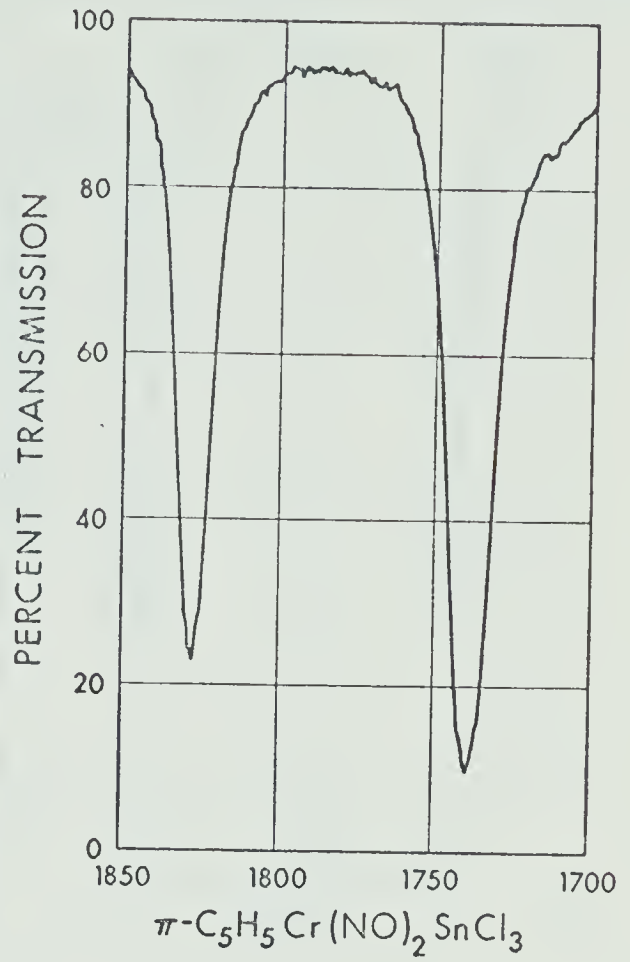


FIGURE 60

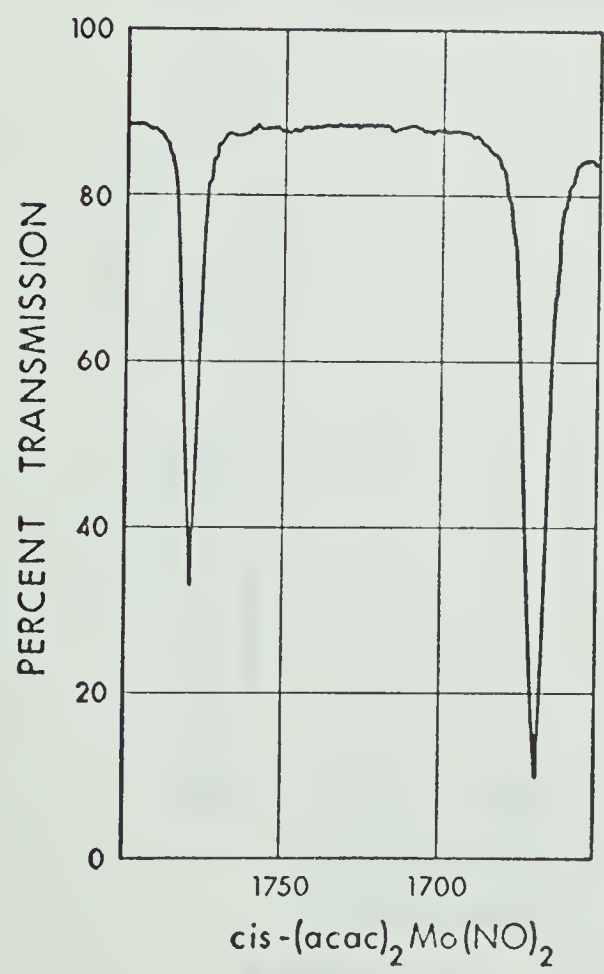


FIGURE 61

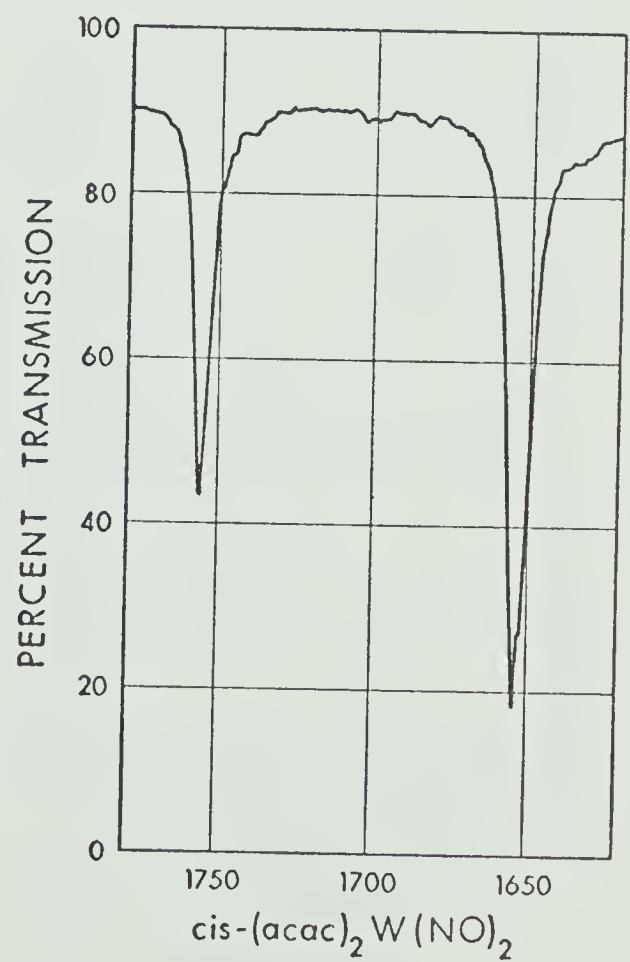


FIGURE 62

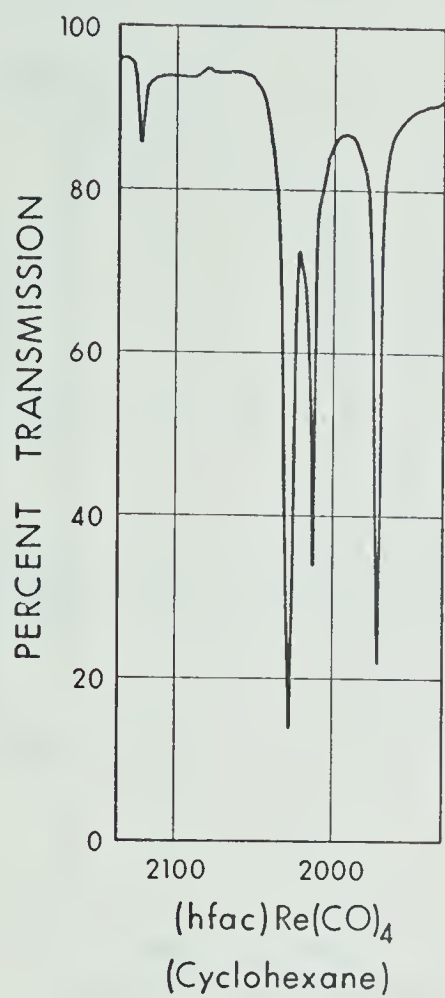


FIGURE 63

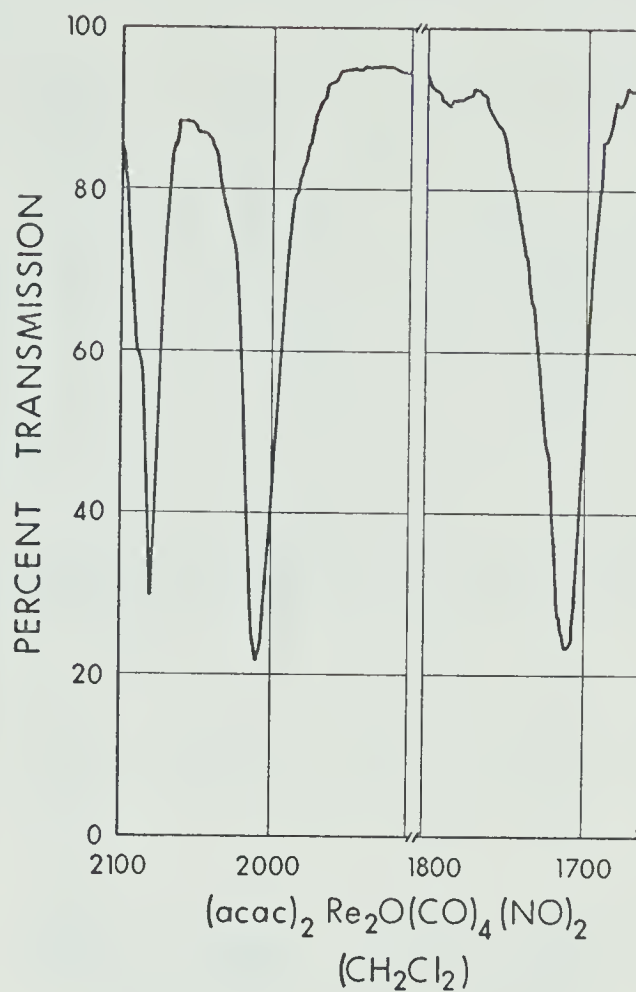


FIGURE 64

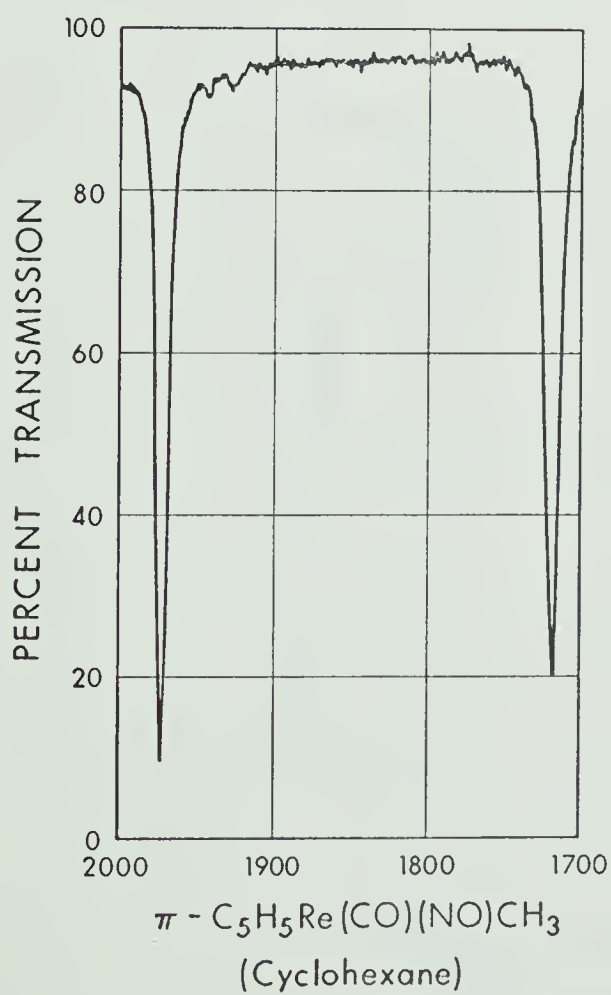


FIGURE 65

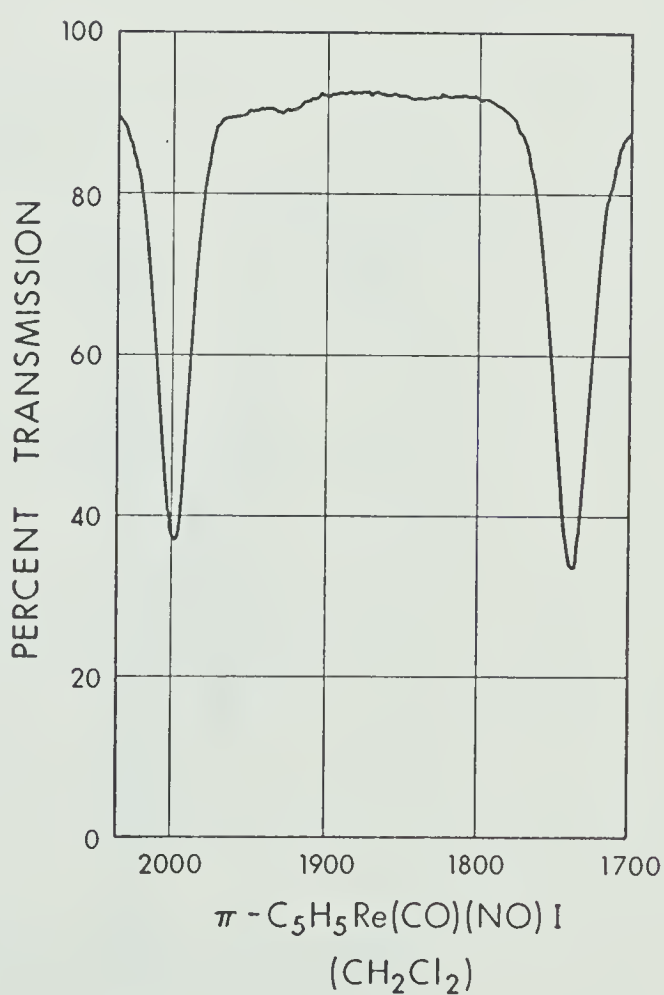


FIGURE 66

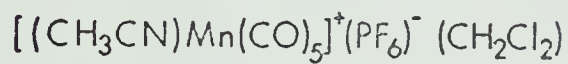
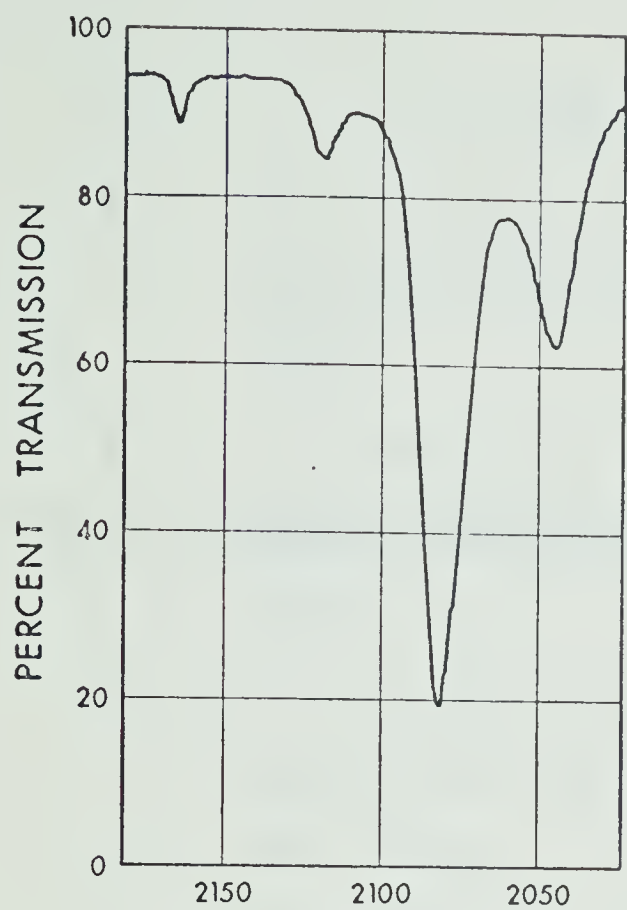


FIGURE 67

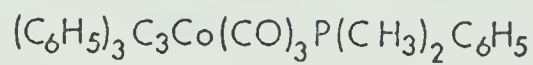
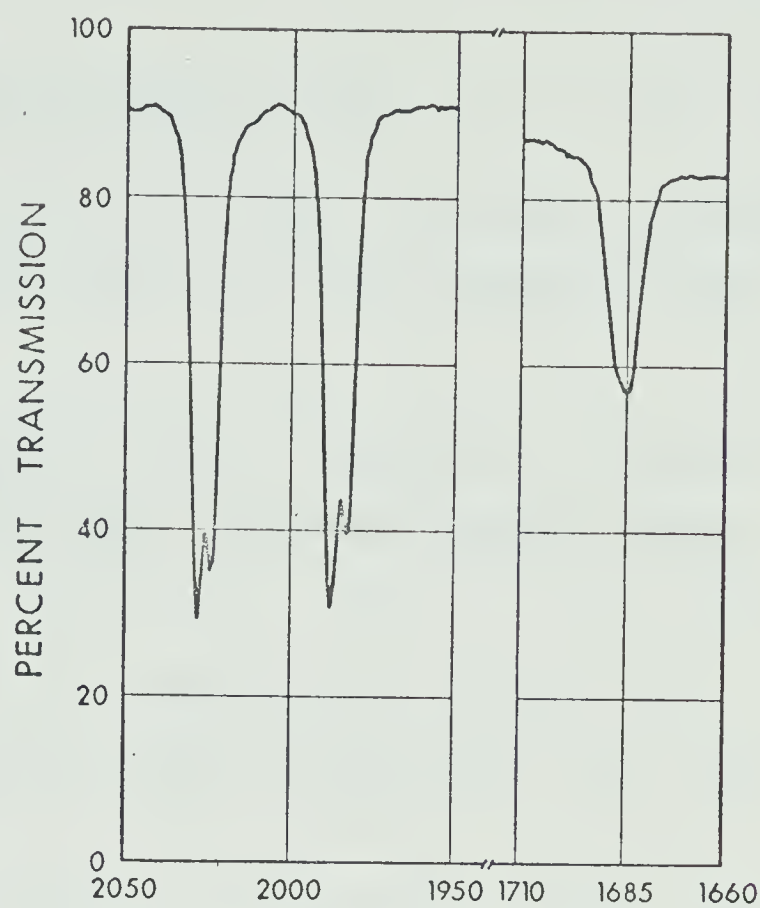


FIGURE 69

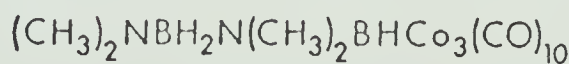
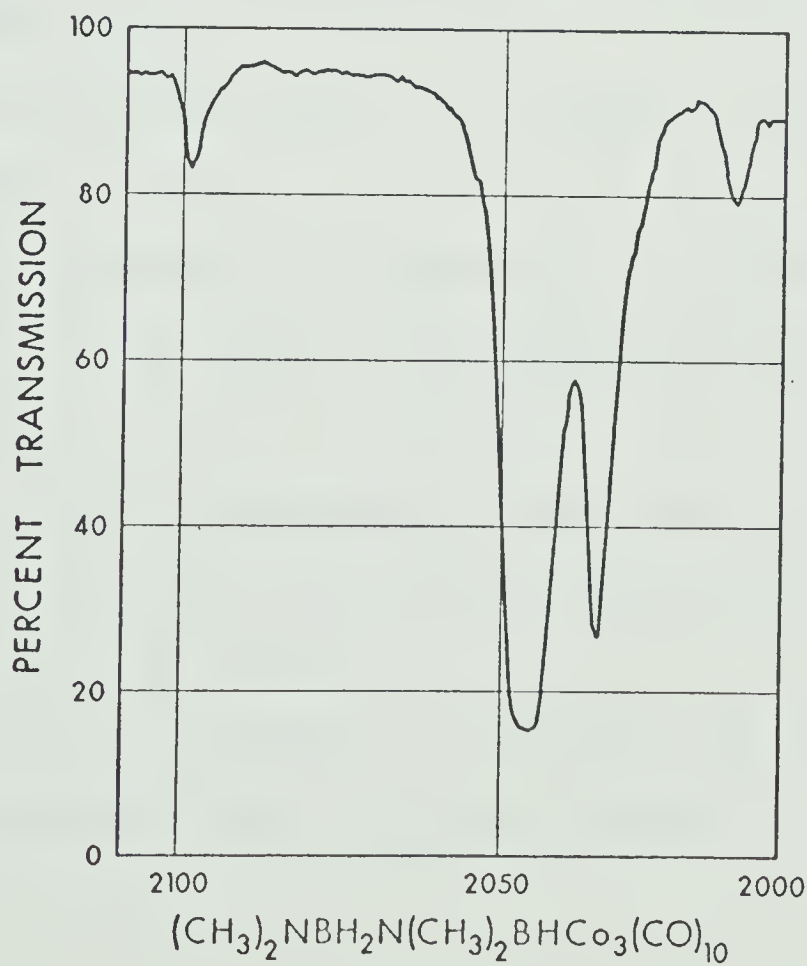


FIGURE 70

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